4-2-2003

Syntheses of single-site catalysts and ethylene copolymers with polar groups

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SYNTHESES OF SINGLE-SITE CATALYSTS AND ETHYLENE COPOLYMERS WITH POLAR GROUPS

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April 2, 2003

A Thesis submitted in partial fulfillment of the requirement for the degree of Master of Science in Chemistry

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Acknowledgements

I would like to express my sincere thanks to my research advisor Dr. Massoud Miri for his excellent continuous guidance, encouragement, and support throughout my research project. My gratitude also goes to my graduate committee, Dr. Marvin Illingsworth, Dr. Andreas Langner, and Dr. Gerald Takacs for their help and support in my graduate thesis research. In addition, I would like to thank Dr. Terence Morrill, Head Department of Chemistry at Rochester Institute of Technologies, who was generous to give me opportunity to finish my master program here. I also thank the Department of Chemistry at Rochester Institute of Technologies for their financial support. I would like to thank Dr. Lenhart from Eastman Kokak Company for his support with H-NMR measurements and Mr. Moody for DSC measurements, and Dr. Nickias from Dow Chemical Company for providing GPC measurements.

I would like to thank my wonderful and lovely American parents Poss and Nadel, who help and support me without condition and always be there when I looked for help. I also would like to say many thanks to my wonderful parents who still live in Viet Nam. I also would like to thank my lovely wife and a beautiful daughter Kimberly who keep me very busy but with a lot of joys. Finally, I would to thank all professors in Chemistry Department, staff in the stockroom, the secretary of the Department of Chemistry, Brenda Mastrangelo, and my all friends from work and school for their continuous support and desire to understand my work.

Abstract

Iron(II) dichloride complexes and iron(III) trichloride complexes were synthesized with a 2,6-bis(imino)pyridyl ligand and obtained in 78.7% and 47.5% theoretical experimental yield respectively. The results of the elemental analysis were in agreement with the expected values. The 2,6-diacetyl pyridine bis(2,4,6-trimethylanil) iron(II) chloride catalysts was remarkable more active than the 2,6-diacetyl pyridine bis(2,4,6-trimethylanil) iron(III) chloride catalyst.

Initially, the catalysts were tested for the polymerization of ethylene, which occurred at relatively high activities (11,158 kg HDPE / mol Fe h [mon]) at 35 ^{o}C. Then we copolymerized ethylene and 1-hexene using iron(III) based catalyst which also led to high activities results. We were able to copolymerize the polar monomer, methylacrylate, with ethylene using the iron(II) based catalyst, and we incorporated close to 1 mol % of methyl acrylate in the copolymer.

GPC results show that the ethylene / methyacrylate copolymers have low polydispersities. TGA, DSC, FTIR, and H-NMR methods were used to characterize the copolymers.

Introduction

Our work involves the polymerization of olefins by using late transition metal, single-site catalysts. We are focusing on the copolymerization of ethylene with methylacrylate as an example of polar monomer via coordinative chain-addition polymerization. Single-site catalysts represent the state-of-the-art Ziegler-Natta catalysts. In contrast, a typical traditional Ziegler Natta catalyst, such as $TiCl_4/AlEt_3$ and γ-$TiCl_3/AlEt_2Cl$ produces more typically several active catalyst sites. The discovery of homogeneous single-site metallocene catalysts, e.g. Cp_2ZrCl_2, at the end of the seventies was a major breakthrough in industry leading to the production of polymers that were superior to the previously produced mass polymers and entirely new types of polymers such as Cycloolefinic copolymers (COC). In the late eighties, another group of single-sites catalysts based on diimine complexes of late transition metals, such as nickel and cobalt, were discovered, which also produce polyolefins at very high activities [1].

High-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), polypropylene (PP), and ethylene-propylene-diene monomer (EPDM) can be produced using Ziegler-Natta type catalysts.

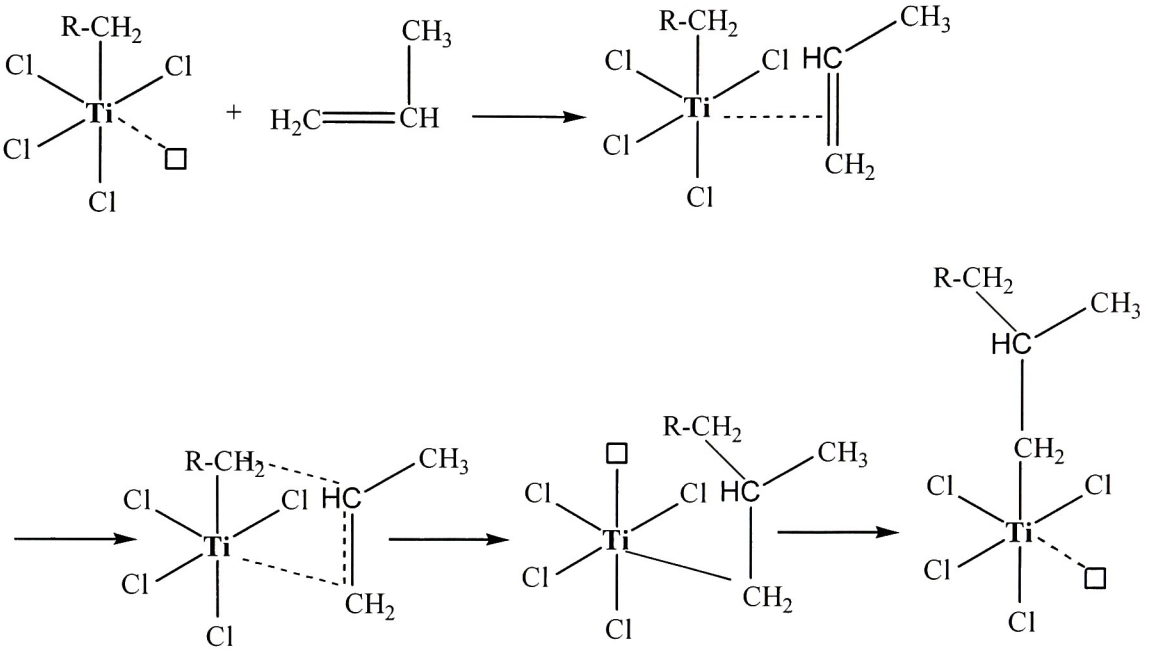
Many types of Ziegler-Natta catalysts have been developed and used for the production of mass polymers. The table below shows the worldwide production of these major types of polyethylene in the past six years [2].

Table 1: Worldwide production of polyethylene.

Polyethylene in millions lbs	1995	1996	1997	1998	1999	2000
LDPE	7,643	7,784	7,691	7,578	8,023	7,987
LLDPE	5,243	6,361	6,888	7,227	9,508	9,907
HDPE	11,211	12,373	12,557	12,924	15,182	15,423

Evolution of Single-Site Catalysts

In 1953, Karl Ziegler discovered that ethylene could be polymerized at moderate conditions in the presence of two metal compounds such as titanium tetrachloride and triethyl aluminum [3]. About a year later, Giulio Natta found that with crystalline modifications of β-and γ-titanium trichloride in combination with diethyl aluminum chloride isotactic polypropylene and other poly-1-olefins could be produced. Ziegler-Natta catalysts typically contain a salt or metal-organic compound of titanium, zirconium, vanadium, chromium, nickel, cobalt, as catalysts, and an aluminum alkyl as cocatalyst [3].



Scheme 1: Mechanistic model of Ziegler-Natta polymerization according to Cossee for heterogeneous Titanium catalyst [3].

For simplification the coordination of the catalyst with the cocatalyst has not been shown in (Scheme1). Initially, to form the active catalyst, an alkyl exchange between the cocatalyst and the transition metal salt must occur, e.g.(Et: ethyl = C_2H_5):

$$TiCl_4 \quad + \quad AlEt_3 \quad \rightarrow \quad TiCl_3Et \quad + \quad AlEt_2Cl$$

The first step shown in (Scheme1) represents the complexation of the monomer to the transition metal complex. Hereby the d-orbitals of the transition metal overlap with the π-bonds of the olefins. The second step shows that an electron deficient four-membered ring is formed. Third, the monomer is inserted between the transition metal atom and the

carbon-atom of the attached alkyl group occurring as a syn-addition. Finally, a "migration" step takes place, in which the alkyl group and the vacant site go back to their original position. In order to obtain an isotactic polymer, the next monomer must undergo complexation and insertion after the migration occurs. With vanadium catalysts, such as $V(acac)_3$, the complexation is faster and a migration will not occur, leading to syndiotactic polypropylene.

In 1965, H. Sinn at the University of Hamburg started research on homogeneous Ziegler-Natta catalysis using simple metallocenes as catalysts such as biscyclopentadienyl titanium dichloride developed earlier by Breslow [4]. These first generation metallocene catalysts have the tendency to produce ethylene copolymers of lower molecular weights. An example of the structure of metallocene compound (Cp_2ZrCl_2) is shown below in figure 1.

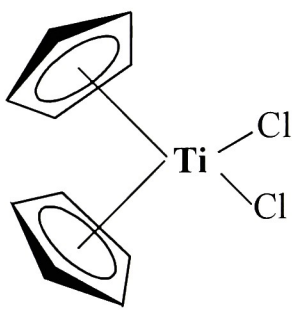
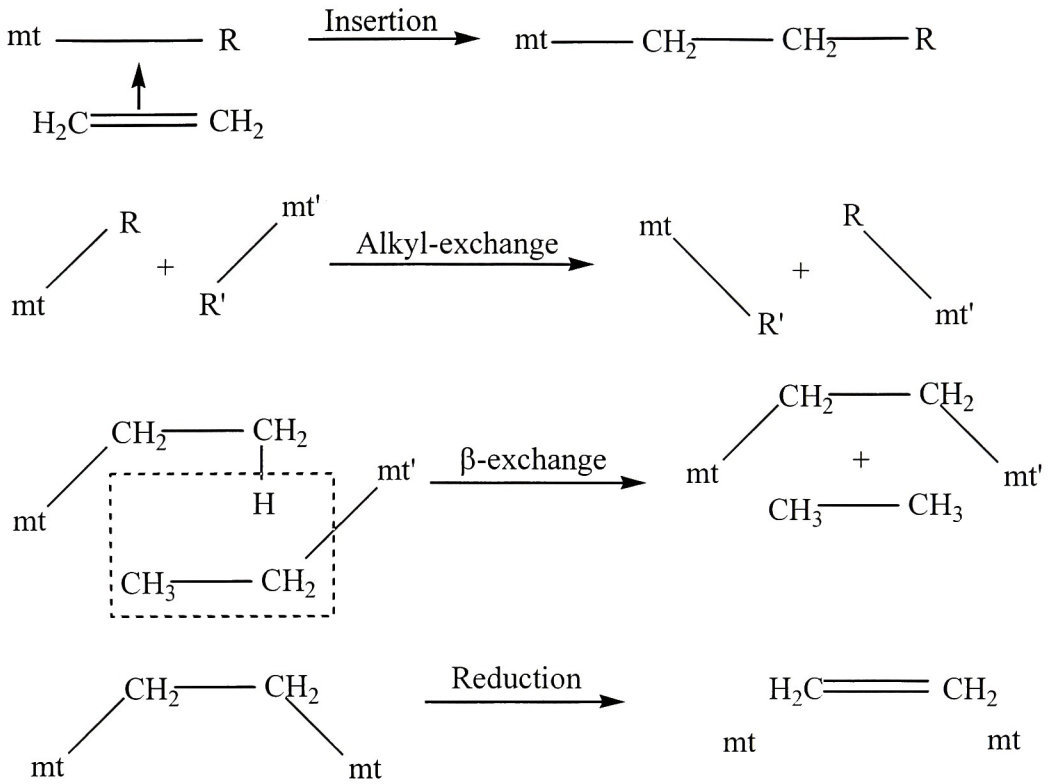


Figure 1: Bis(cyclopentadienyl) titanium dichloride [4].

Sinn chose these soluble catalysts because they appeared more feasible for kinetic studies. Later, he and Kaminsky studied the structures of the catalyst compounds and their reactions with ethylene. Their detailed kinetic studies that took close to 15 years are summarized in Scheme 2.

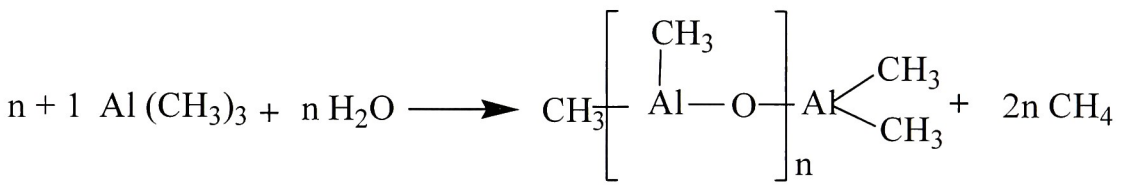


Scheme 2: Mechanism of Ziegler-Natta polymerizations including side-reactions [4].

The first step is the fast complexation and insertion of the monomer as part of the desired polymerization. A β-hydrogen atom is transferred from the alkyl group of the other transition metal resulting in the evolution of ethane, and this step proceeds to the ultimate reduction and deactivation. It also had been found that a high amount of halogen typically in the cocatalyst enhances the reduction of the transition metal. Furthermore, zirconium has a lower tendency to reduction than titanium. Accordingly, the perfect combination for a Ziegler-Natta system should be $Cp_2Zr(CH_3)_2$ with $Al(CH_3)_3$, because the side reactions leading to catalyst deactivative would be minimal.

However, it turned out that this combination was not active for polymerization of ethylene. Accidentally, students who were less experienced with Schlenk systems to protect the catalysts compounds from poisons such as oxygen and water, managed to obtain higher polymer yields.

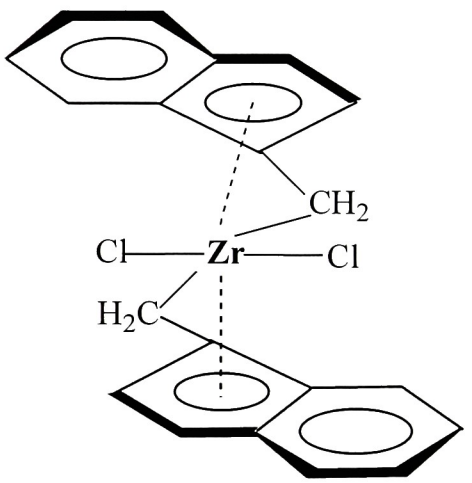
Sinn and Kaminsky discovered that relatively small amounts of water, which were present in the moisture in the air, reacted with trimethylaluminum to form a more active catalyst system. For subsequent polymerizations they first produced the reaction product of the aluminum alkyl and water, called methylaluminoxane (MAO), and used the new isolated compound as cocatalyst, according to the following reaction:



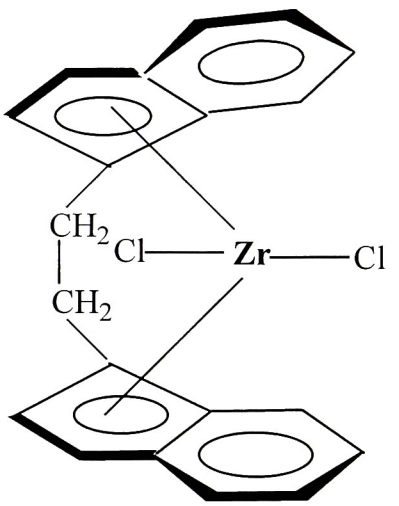
This new cocatalyst boosted the activities to unprecedented high levels and the so-called first superactive metallocene catalyst had been found as a combination of Cp_2ZrMe_2 with MAO [4].

This was the first Ziegler-Natta catalyst that did not contain a halogen atom, which had been considered a prerequisite for catalyst activity. The activities of the first metallocene generation catalysts exceeded in many cases those of the best industrial Ziegler-Natta catalysts, e.g. 30,000 kg PE /gZr. It could be also demonstrated that other monomers could be copolymerize with ethylene such as 1-hexene, forming LLDPE (Linear Low Density Polyethylene), and with propylene leading to EPDM (Ethylene/Propylene/Dienmonomer) elastomers [5]. However, these early metallocene catalysts only produced atactic polypropylene (at-PP).

In 1985 both Ewen at Exxon and Kaminsky discovered that chiral and rigid metallocenes led to the formation of isotactic polypropylene. Such catalysts had been synthesized by Brinzinger at the University of Konstanz, for example ethylene bis (indenyl) zirconium dichloride shown below. These bridged metallocene catalysts typically result also in polymers with higher molecular weights [6].



Racemic form (it-PP)



Meso-form (at-PP)

Figure 2: Ethylene bis(indenyl) zirconium dichloride [6].

The catalyst compound contains a two-ring system made of a cyclopentadienyl ring fused to a phenyl ring called indenyl and an ethylene bridge connected to the aromatic ring ligands. Without the ethylene bridge, the ligands swivel around and might not stay pointed in the right direction to lead to isotactic polymerization. The big bulky indenyl ligands point in opposite directions as they are guiding the incoming monomer for the insertion.

Only the racemic mixture or enantiomers results in high degrees of isotactic polypropylene, however the meso-form form leads to atactic polypropylene. The racemic form of the catalyst has a C_2-symmetry and its mirror images, function in an analogous manner as the neighboring enantiomeric sites in a $TiCl_3$ crystal. As shown in Figure 3, it does not matter from which side the monomer is approaching the specific enantiomer, which could e the R or S form. The propylene always approaches the specific catalyst site with the same enantiotropic face, i.e. Re-face or Si-face [6].

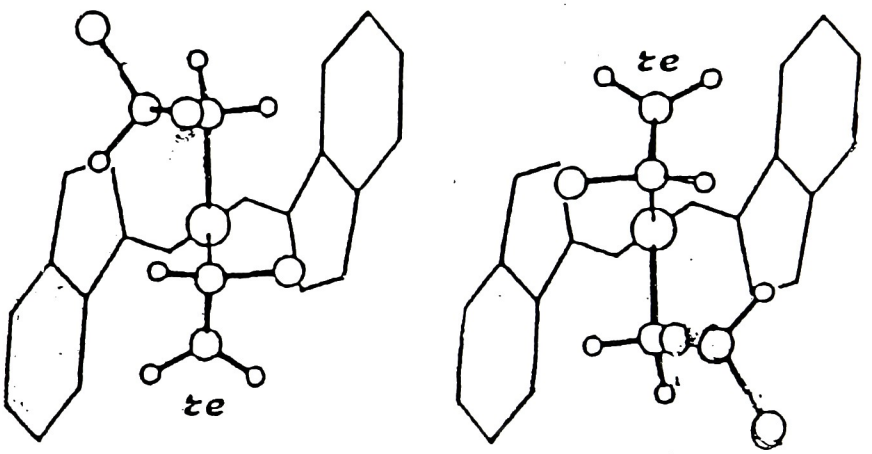


Figure 3: Addition of propylene to the active catalyst, ethylene bis(indenyl) zirconium dichloride [6].

Consequently for the first time highly crystallinity polypropylene had been produced with a soluble Ziegler-Natta catalyst. This was a major breakthrough for the commercialization of metallocenes as catalysts for the production of the major common polyolefins.

Later, Ewen and Razavi designed rigid fluorenyl cyclopentadienyl zirconium catalysts, and with these catalysts highly syndiotactic polypropylene could be produced. The fluorenyl catalyst has a C_s-symmetry with a mirror plane going horizontally through the molecule as shown in figure 4. The bulky wings of the fluorenyl ring force the methyl group of the incoming propylene in between the two six rings of the fluorenyl group. On one side of this catalyst the Re-enantiotopic face will be added, and the Si-face on the opposite site. Since with every insertion the polymer chain changes its position syndiotactic polypropylene will be formed. When a bulky group such as a tertiary butyl group is present at the β-position, the propylene is forced to add only from one side and racemic it-PP is formed [6].

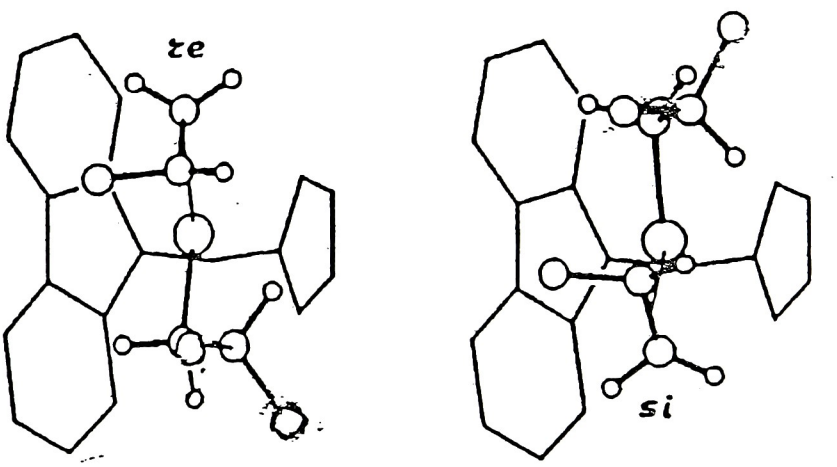


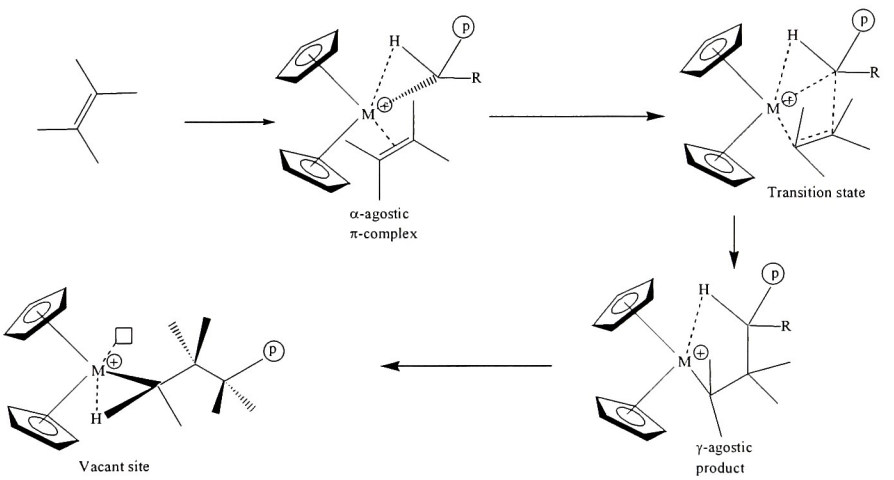
Figure 4: Models for the stereocontrol of olefin insertions in fluorenyl containing zirconium catalysts with Cs-symmetry proposed by Corradini [6].

The cocatalyst methyl aluminoxane (MAO) plays an important role for metallocene catalysts. The methyl group from MAO is necessary for the alkylation of the catalyst, and abstracts chlorine giving the zirconium a positive charge, see structure below. This charged complex is stabilized because the electrons from the carbon-hydrogen bond are shared with the zirconium.

The following reaction shows how the catalyst works with co-catalyst to yield the cation complex formation.

$$Cp_2ZrCl_2 \quad + \quad MAO \longrightarrow \quad Cp_2ZrCl^+ \quad + \quad [MAOCl]^-$$

The Cossee-Arlman mechanism applied for metallocenes below explained how the cocatalyst works.



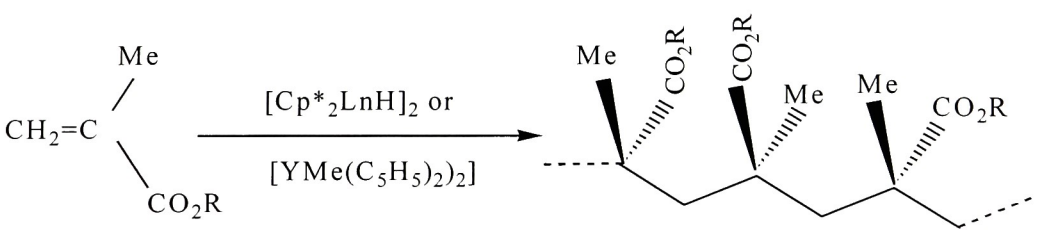
Scheme 3: Cossee-Arlman mechanism for metallocene polymerization [7].

For simplification, the cocatalyst (MAO) is not shown here, but the alkylation stage took place prior to complexation step. In the first stage, an α-agostic hydrogen and π-complex help to make the complex more stable. Then a four-membered ring is formed, and the complex becomes electron deficient. When the bond is rearranged an γ-agostic product is

formed. The complex flips back with a vacant site and in the opposite position to the reagent in the first reaction step. With every insertion the polymer chain flips back to the other side and the vacant site also changes sides compared to the active catalyst at the beginning of the previous insertion step.

It has been quite difficult to polymerize polar monomers, such as 5-hexene-1-ol or methyl methylacrylate using metallocene catalysts. Typically these polar compounds lead to a deactivation of the catalyst system. Indeed, alcohols are used to quench polymerizations. It is assumed that some polar compounds establish bonds with the metallocenes that prevent them from the complexation and insertion steps of the basic polymerization. In particular, the presences of strong acids result in the formation of aluminum compounds, which are ineffective for the polymerization. High amounts of water also can hydrolyze the metallocenes.

Metalorganic compounds of rare earth metals, such as samarium and yttrium, have been shown to be suitable catalysts that polymerize polar monomers, such as methyl methylacrylate by Yasuda. [8a, b]



R = Me, Et, i-Pr, t-Bu
Ln = Sm, Yb, Lu

Mn >5.0 x10^5, Mw/Mn<1.05

In another study by Yasuda, high molecular weight PMMA with narrow polydispersity were obtained by using $[SmH(C_5Me_5)_2]_2$ and $LuMe(C_5Me_5)_2(THF)$ catalysts [8a]. Table 2 below shows some data of this work.

Table 2: Data for polymerization with a rare earth transition metal catalyst [8a].

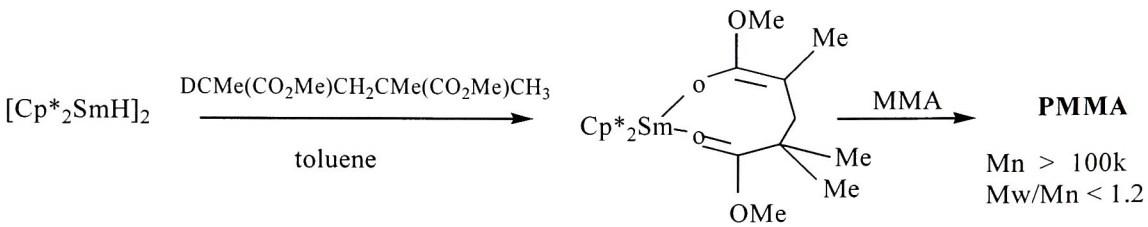
Initiator	Monomer [b]	10^{-3} x Mn	Mw / Mn	rr in %	Conversion in %
$[SmH(C_5Me_5)_2]_2$	MMA	57	1.03	82.4	98
$[SmH(C_5Me_5)_2]_2$	EtMA	80	1.03	80.9	98
$[SmH(C_5Me_5)_2]_2$	iPrMA	70	1.03	77.3	90
$LuMe(C_5Me_5)_2(THF)$	MMA	61	1.03	83.7	98

[a] Polymerization conditions: O°C in toluene, initiator concentration: 0.2 mol%

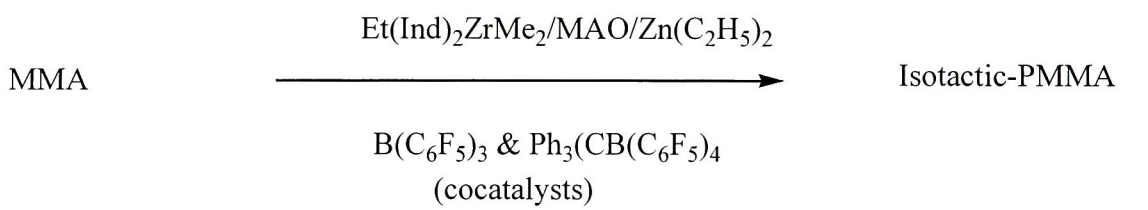
[b] EtMA: ethyl methacrylate; iPrMA: isopropyl methacrylate; tBuMA: tert-butyl methacrylate.

As the bulkiness of the alkyl group increased the syndiotacticity of the methacrylate group also decreased. The organolanthanide complexes cause the formation of polymers to high conversions within a short time period, and due to a wide range of polymerization temperatures at lower temperatures 95 % of syndiotactic polymer was obtained. The rare transition metal compound $Me_2Si(C_5Me_5)$ $(C_5H_4$-1S,2S,5R-neomenthyl)LaR (R = $CH(Me_3Si)_2$ produced isotactic poly(methyl methacrylate) [8b]. However, these catalysts are also more sensitive to moisture and generally not as stable as most metallocenes, which is the cause for their lower polymerization activities.

In 1992, Yasuda and Yamaoto employed 3B group lanthanide complexes $[Cp^*_2SmH]_2$ and $[YMe(C_5H_5)_2]_2$, and they obtained syndiotactic polymers with an extremely narrow molecular weight distribution (MWD = 1.05 – 1.02) [8c].



In 1994, Soga and his coworker initially formed a complex of a Lewis acid such as diethyl zinc $[Zn(C_2H_5)_2]$ with the methyl methyl acrylate monomer. This activated initiator was then used with a metallocene catalyst to form the isotactic-PMMA [9].



The role of diethyl zinc in the reaction is to prevent deactivation of the metallocene metal center through the strong interaction of the additive with the functional ester group of monomer. This combination allowed the usage of a lower amount of MAO.

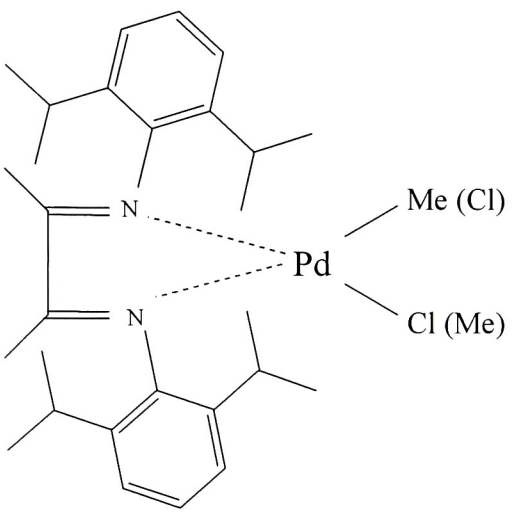
Also in 1992, Collins and Ward produced syndiotactic poly(methyl methacrylate) at moderate activities with a narrow molecular weight distribution by using Cp_2ZrMe_2 and $[Cp_2ZrMe(THF)][BPh_4]$ at room temperature. Later, they found out that polymerization was initiated by those complexes that developed effective initiators for living polymerization of methyl methacrylate. [10a]

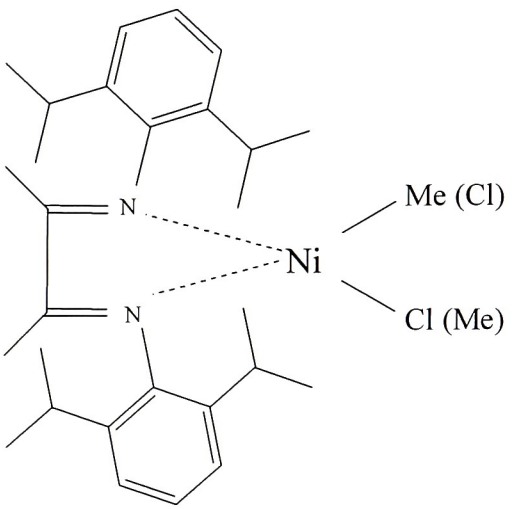
In another study, Collins and Ward showed that metallocenes catalysts could polymerize methyl methacrylate by using Cp_2ZrMe_2 at room temperature and a highly syndiotactic PMMA can be produced with molecular weight of (Mw = 50 – 200,000 g/mole), and molecular distribution (MWD = 1.2 – 1.4) [10b].

Ethylene / methylacrylate copolymers provide more useful materials to our society today. Their applications are not only used to protect citrus trees from frost damage, but also lubricating oils, additives, surface coatings, impregnates, adhesives, binders, sealers, and floor polishes (Exxon Mobil). It is impossible to segregate the total copolymers with acrylates and other monomers.

The Exxon Mobil Chemical Company produces a series of ethylene / methylacrylate copolymers called OPTEMA [11]. These OPTEMA TC020 and TC120 are used for seaming, heavy-duty shipping sacks, pond liners, medical packages, agricultural, and construction films [11].

In the late 80's Brookhart discovered that the use of palladium(II) and nickel(II) based catalysts lead to polymerization of ethylene and of propylene at high activities [12].

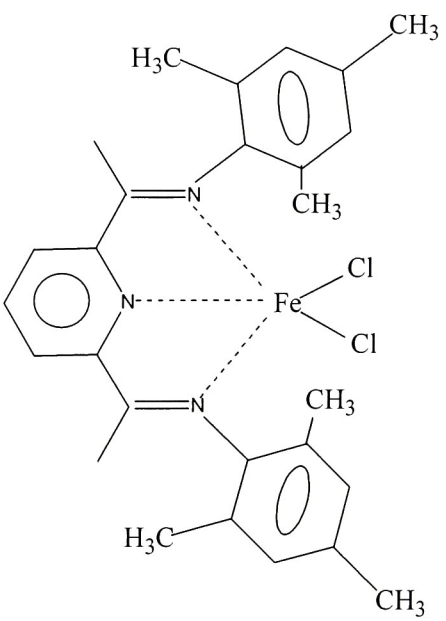


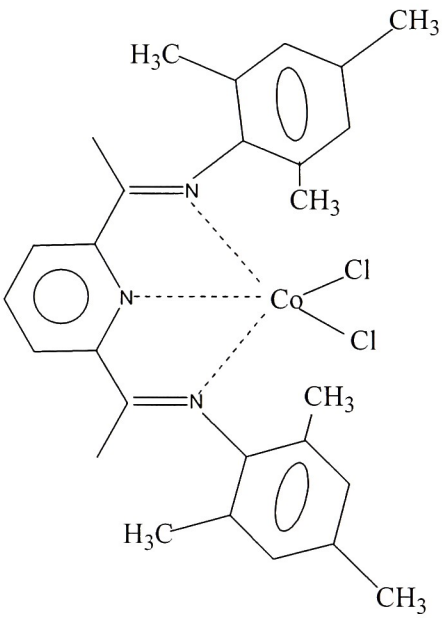


These α-diimine catalysts also produced poly-α-olefins of high molecular weights and afford living copolymerization of 1-olefins to block copolymers. Due to the nature of late transition metal catalysts, they are expected to be more tolerant towards functionalized vinyl monomers. According to Correia only Pd(II) with α-diimine ligands could catalyze copolymerization of ethylene with a functional monomer and with monomers that do not have acidic hydrogens [13].

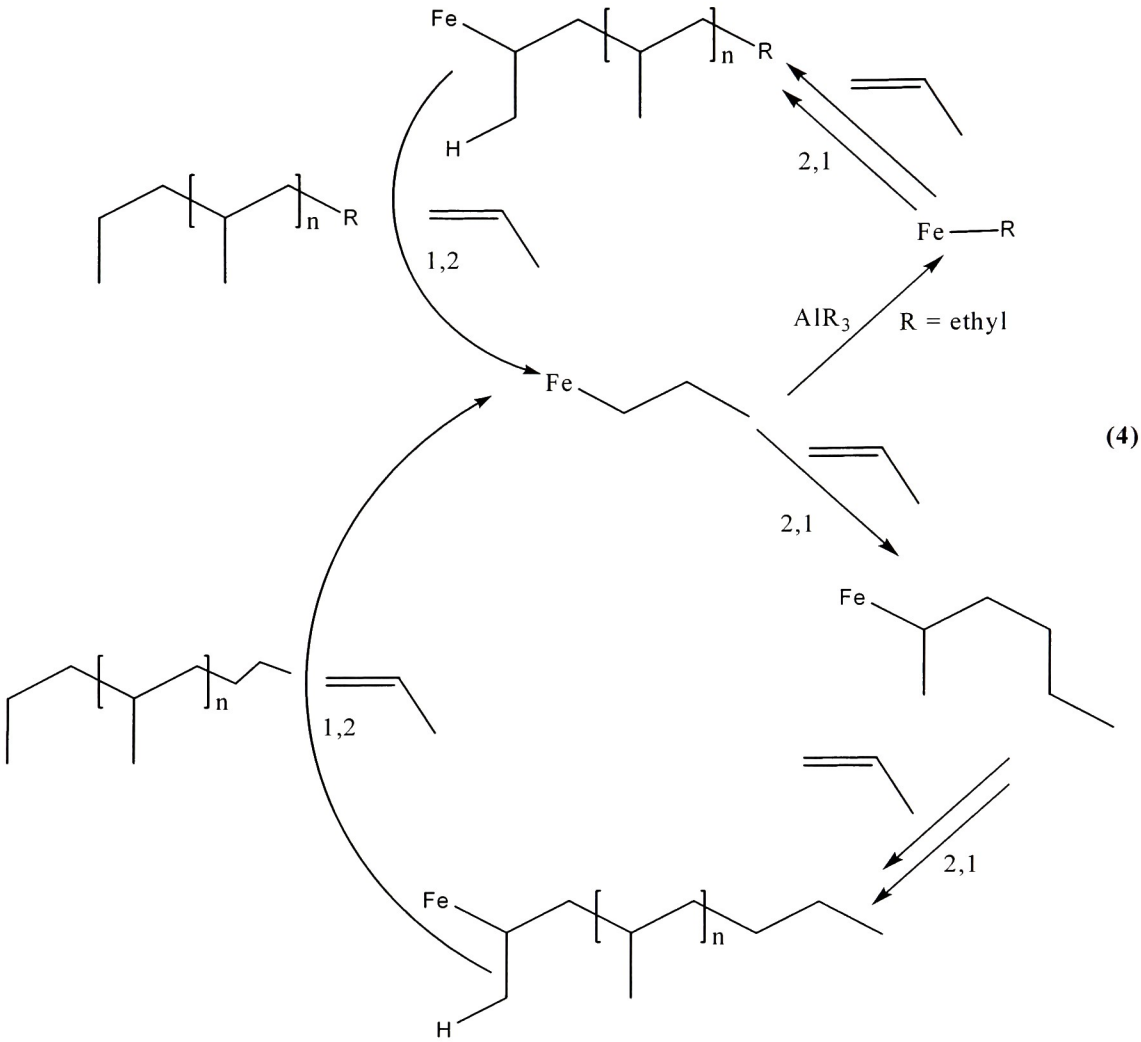
Late transition metal such as Pd(II) and Ni(II) were incorporated with α-diimine ligands to produce the high molar mass polymers for both ethylene and 1-olefins. The most unique features of these late metal include the ability to produce highly branched ethylene polymers and potentially copolymerize ethylene with other polar monomers.

Recently, Gibson and Brookhart groups discovered new catalysts based on pyridine-diimine complexes of Fe(II) and Co(II) [14].





They could be even less electrophilic and oxophilic than the α-diimine complexes of Ni(II). At the end of the ninetees, Brookhart and Gibson [14] published that iron(II) & (III) and cobalt(II) complexes with 2,6-bis imino pyridyl ligands were highly active. These later catalysts have a good potential to be active for our target polymers. The iron complexes reported herein in (Scheme 4) represent a new class of isospecific propylene polymerization catalysts [15].

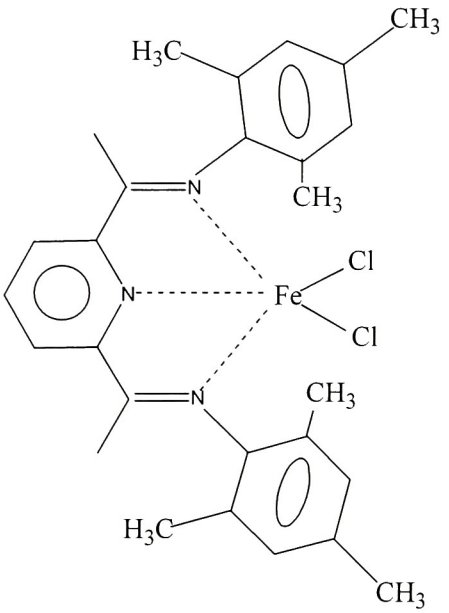


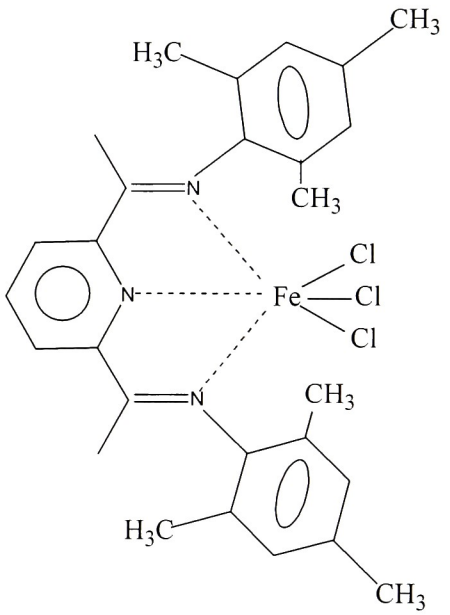
(4)

Scheme 4. Brookhart's mechanism of Initiation, Propagation, and Termination [15].

These catalysts are unique in several ways. First, they are the first late-metal systems known to polymerize propylene in an isotactic fashion. Regardless of catalyst structure, the isotacticity is governed by a chain-end control mechanism. Second, chain propagation proceeds through 2,1 insertion of monomer, making these the first isospecific propylene polymerization catalysts that operate via a secondary enchainment mechanism. Third, the polymer end groups resulting from termination consist solely of

1-propenyl groups, making these the first systems to produce only α-olefin end groups by β-H elimination from the growing polypropylene chains. Finally, these polymers are highly regioregular, with regioerrors occurring only in the lower molecular weight polymers made by the complexes with reduced steric bulk.





Synthesis of bidentate Fe(II) and tridentate Fe(III) complexes demonstrated the extremely active and long-lived catalysts for ethylene polymerization.

Copolymerization Theory

One important property of a copolymer is its composition, which is expressed typically as fractions of each monomer based on the monomer units in the copolymer of the monomers, $n_A + n_B$, for example $F_A = n_A / (n_A + n_B)$, or as the ratio F_A/F_B. Another important property of copolymer is its monomer sequence distribution, and the three representative examples are shown below:

Type of Monomer Sequence Distribution in Copolymer	**Representative Sequence**
Alternating	ABABABABAB
Random	BAAABBABBA
Block	AAAAABBBBB

In typical binary copolymerizations, only one of the terminal monomer units of the growing polymer chain has an effect on the rate.

According to the "Terminal Model", these are four basic propagation reactions:

$$-A^* + A \xrightarrow{k_{AA}} -A-A^*$$

$$-A^* + B \xrightarrow{k_{AB}} -A-B^*$$

$$-B^* + A \xrightarrow{k_{BA}} -B-A^*$$

$$-B^* + B \xrightarrow{k_{BB}} -B-B^*$$

Based on the rate laws, one can express the relative monomer ratio as:

$$\frac{-d[A]/dt}{-d[B]/dt} = \frac{k_{AA}[A^*][A] + k_{AB}[A^*][B]}{k_{BB}[B^*][B] + k_{BA}[B^*][A]}$$

Assuming steady-state conditions, and using $r_A = k_{AA} / k_{AB}$ and $r_B = k_{BB} / k_{BA}$ one obtains:

$$\frac{d[A]}{d[B]} = \frac{[A]\, r_A\, [A] + [B]}{[B]\, r_B\, [B] + [A]}$$

This is one form of the so-called "Copolymerization Equation" of Mayo and Lewis [16]. Each r-value refers to one type of terminal monomer and it is called "reactivity ratio". This equation is only valid for the initial compositions at low monomer conversions. To construction a copolymerization diagram with monomer fractions, f_I for the feed compositions on the abscissa, and F_I for the copolymer composition on the ordinate, it is more useful to use this form of the equation.

$$F_A = \frac{r_A f_A^2 + f_A f_B}{r_A f_A^2 + 2 f_A f_B + r_B f_B^2}$$

The simple relation of the product of reactivity ratios, $r_A \times r_B$, and the type of copolymerization and the monomer sequence distribution is shown below.

Reactivity Ratio Product	Type of Copolymerization	Comparision of Composition in Feed vs. Copolymer	Monomer Sequence Distribution
$0 \leq r_A \times r_B < 1$	Alternating	Different, except for azeotrop	Alternating
$r_A \times r_B = 1$	Ideal	Different, unless $r_A = r_B = 1$	Random
$r_A \times r_B >> 1$	Block	Different, except for azeotrop	Block

We used an in-house software program to create diagrams for binary copolymerization [17]. The Fineman-Ross equation below was used to calculate the reactivity ratios of the copolymer [18].

$x(1 - 1/y) = r_1(x^2 / y) - r_2$

Where $x = [M_1]/[M_2]$, $y = d[M_1]/d[M_2]$, so that the equation becomes:

$y = x(1+r_1x)/(r_2+ x)$

Research plan

Initially, I planned to reproduce and modify the synthesis of iron(II) and (III) catalysts by using Brookhart and Gibson procedures. I also included in my plan to synthesize ruthenium(III) chloride complexes with the (divinyl pyridyl) ligands according to the same produces described above.

Once we were successful in synthesizing the metalorganic compounds, we planned to use them as polymerization catalysts with ethylene, followed by a few copolymerizations with 1-hexene. As polar monomers to be copolymerized with ethylene, we selected 5-hexene-1-ol and separately methylacrylate. Our plans also entailed the determination of the properties of the obtained polymers.

Experimental

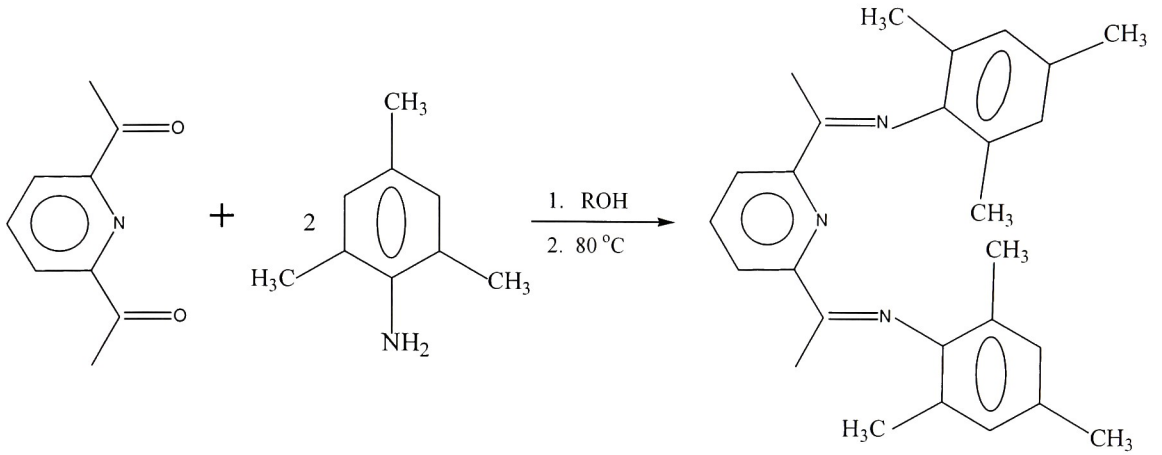
Synthesis of Catalyst Compounds

Preparation of Reagents

All reagents and solvents were acquired from the Aldrich Chemical Co., with the exception of ethylene, which was obtained from Matheson, and methylaluminoxane obtained as 10wt% solution in toluene from Witco. All reagents and solvents were manipulated using Schlenk-tube techniques using argon as inert gas.

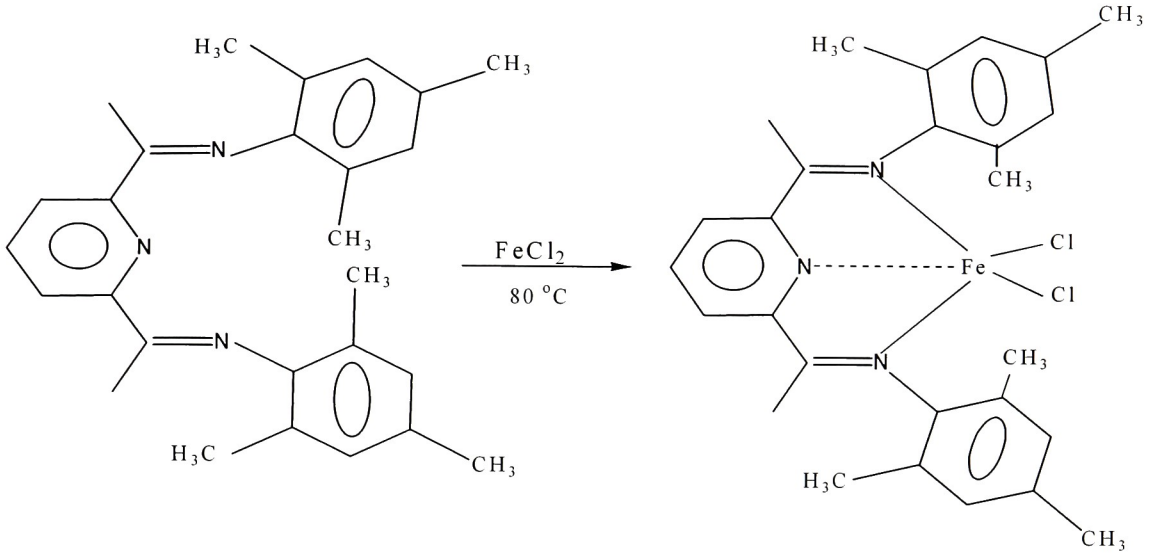
Toluene was refluxed and distilled over sodium/benzophenone over night prior to use. Monomers and diethyl ether were degassed, refluxed over calcium hydride over night, and distilled. Other solvents or liquid reagents were dried over 3A molecular sieves, which had been previously heated at 200 ^{o}C under vacuum for 24 hours.

A.1. Synthesis of 2,6-bis(imino) pyridyl ligand



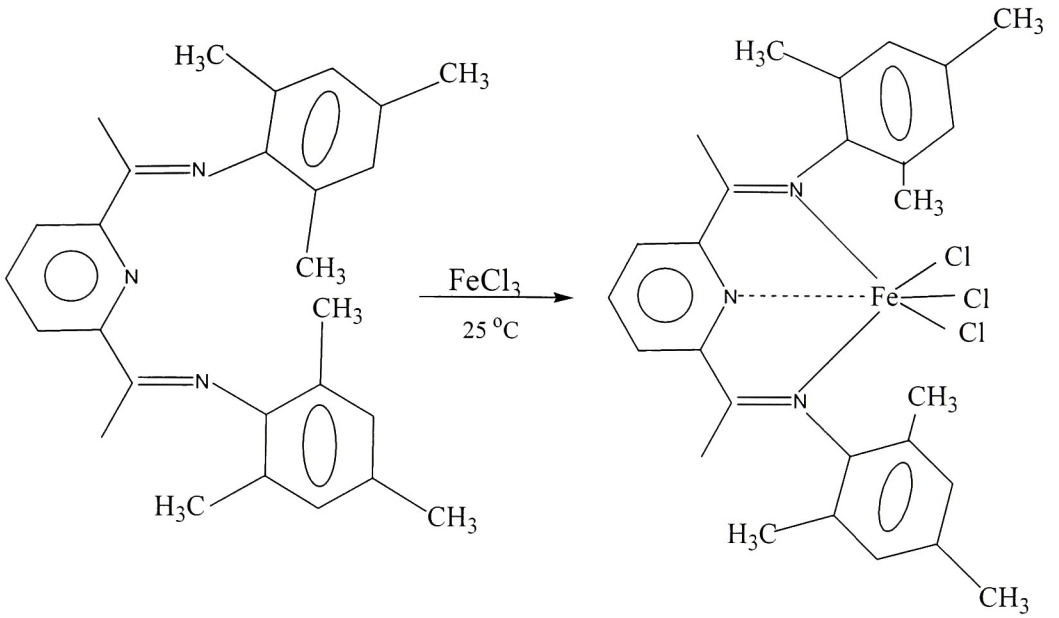
To a three-neck flask, which had been heated and evacuated three times with argon, 3.0g (18.4 mmol) of 2,6-Diacetylpyridine were dissolved in 50 mL ethyl alcohol. 20.6 mL (36.8 mmol) of 2,4,6-Trimethylaniline were added to this solution. The flask was equipped with a magnetic stirrer and thermometer. 10 drops of glacial acetic acid were added, and the solution was refluxed at 80 °C for 24 hours. The solution became red-purple. The flask was placed in an ice bath one day. The resulting precipitate was washed with cold ethanol, and the yellow solid formed was isolated by filtration. The product was then dried over night in vacuum. 5.38g of the product were obtained equal to 74.5% of the theoretical yield.

A.2. Synthesis of polymerization catalyst I



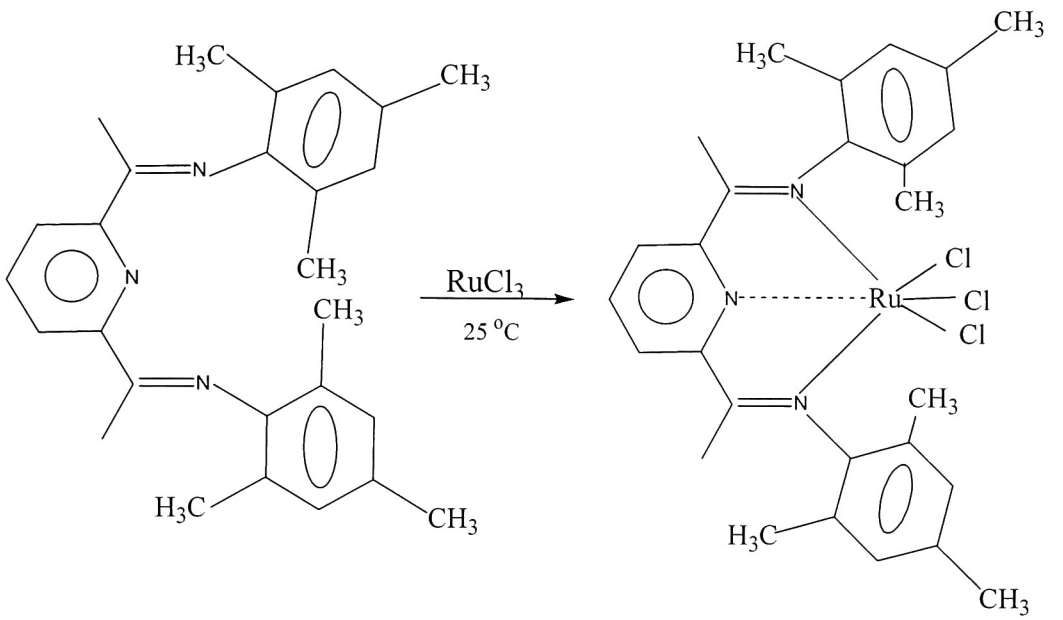
To a three-neck flask, 0.24g (1.89 mmol) of $FeCl_2$ were dissolved in 20 mL of n-butanol and stirred at 80 °C in an oil bath for one hour until all solid had completely dissolved. 0.75g (1.89 mmol) of the ligand produced in (A.1) was suspended in 10 mL of n-butanol. According to the literature procedure [14], one has to start to add the suspension drop-wise into the solution that contained $FeCl_2$. However, this technique did not work out well, because the solids plugged the inlet tube and a needle had to be used to push the solids down to the reaction flask. In order to make the procedure more convenient and efficient, I mixed $FeCl_2$ with n-butanol and stirred the solution at 80 °C until the entire solid had dissolved and then I added the solid ligand directly in small portions to the solution. The solution's color changed to dark blue. It was stirred for another 15 minutes, then cooled down to room temperature and concentrated by pulling vacuum. 30 mL of diethyl ether was added to the solution and a dark blue solid formed which was isolated by filtration. The product was then dried in vacuo over night and gave as dark blue solid. This method gave 1.04g of the product and equal to 78.7% of the theoretical yield.

A.3. Synthesis of polymerization catalyst II



To a three-neck flask, 0.11g (0.62 mmol) of $FeCl_3$ were added followed by 80 mL of acetonitrile and the solution stirred at room temperature until the entire solid dissolved leading to a dark blue color solution. 0.26g (0.62 mmol) of ligand (prepared in A 1) was added as a solid directly to the solution contained $FeCl_3$, and stirred over night at room temperature and a precipitate was formed. To the resulting product 60 mL of diethyl ether were added and the mixture was filtered. The product was then dried in vacuo over night and gave 0.16g of product as dark blue solid corresponding to 47.5% of the theoretical yield.

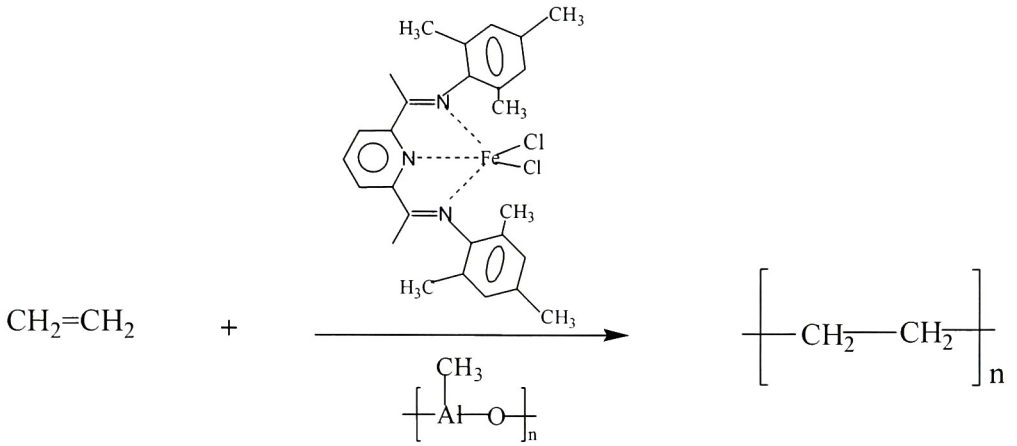
A.4. Synthesis of polymerization catalyst III



To a three-neck flask was added 0.13g (0.62 mmol) of $RuCl_3$, followed by 80 mL acetonitrile. The solution then was stirred at room temperature until the entire solid completed dissolved and the color of the solution was dark brown. 0.26g (0.62 mmol) of ligand were added directly to the solution, and the solution was stirred for over night. A precipitate was formed and 60 mL of diethyl ether were added to the solution and filtered. The product was then dried in vacuo overnight and gave a blackish solid in 0.08g corresponding to 23% of the theoretical yield (Later elemental analysis revealed that the product was mainly unconverted $RuCl_3$).

General polymerization procedures

B.1. Example of a polymerization of ethylene using $FeCl_2$ based catalyst:



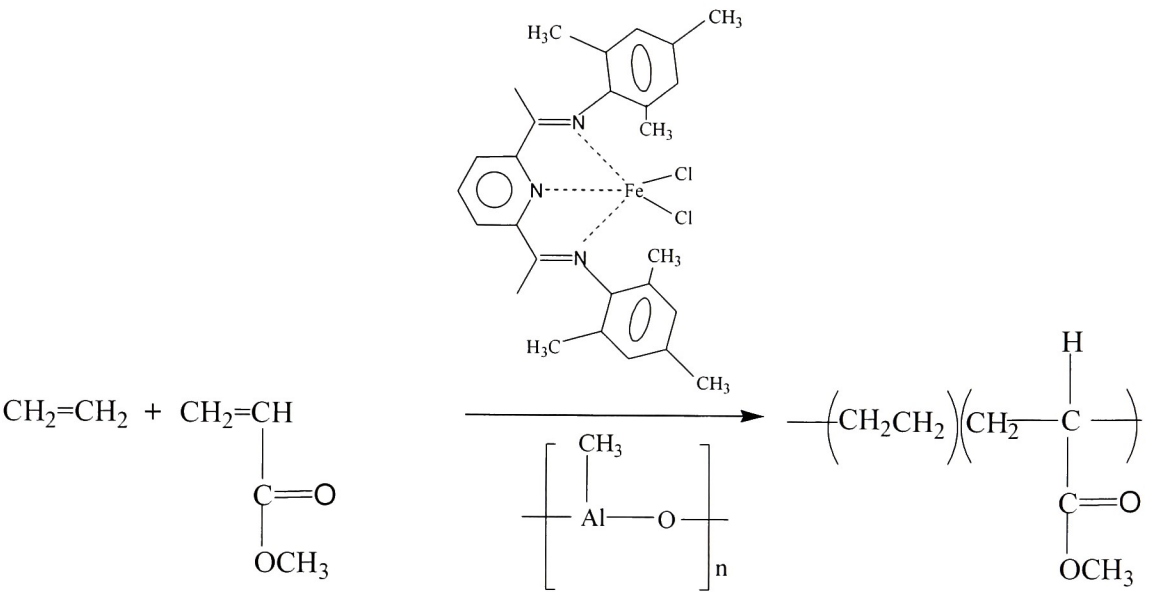
A1-L Buchi reactor was heated under vacuum and back filled with argon three times for 45 minutes at 70 °C. The temperature was reduced to the desired polymerization temperature i.e. 20 °C. The temperature was measured via a thermoelement in the vessel, which was directly connected to the heater of the circulating bath. Manual cooling was applied when the polymerization temperature increased above 1 °C due to the exotherm.

Then the vessel was charged with 248 mL of distilled toluene, and followed by 1 mL of a 10wt% in toluene (= 1.7×10^{-3} mol) of methylaluminoxane as solution. The reactor then was pressurized to 38 psi (2.0 bar) atmosphere and the stirrer speed adjusted to 600 rpm. The solution was then saturated with ethylene for about 10 minutes before the catalyst introduced. 0.16 mg (2.05×10^{-7} mol) of catalyst was added as a solid suspension in 1 ml of toluene via a syringe, bringing up the volume to a total of 250 mL and the solution stirred. The amount of ethylene consumed was recorded with a flow meter. To terminate the polymerization about 50 mL ethyl alcohol was added and the polymer was collected by filtration. After stirring with diluted hydrochloric acid over night and filtering, the solid polymer was dried in an oven at 70 °C and 3.5g of polyethylene were obtained.

B.2. For the ethylene/1-hexene copolymers and ethylene / 5-hexene-1-ol copolymer.

Essentially the same procedures as above was used with the exception that after the addition of the toluene (the volume of whole was reducing by that of the hexene) the hexene was added (e.g. 13.5 mL = 0.428 mol) and 3.66g copolymers were obtained. The same procedure was used for polymerization of ethylene / 5-hexene-1-ol (3.9 mL = 0.13 mol) and no polymer was obtained.

B.3. As a normal polymerization of ethylene and methylacrylate with $FeCl_2$ and MAO premixed catalysts (e.g. E/MA Cop4)



A 1L Buchi reactor was heated under vacuum and back-filled three times with argon for 45 minutes at 70 °C. The temperature was reduced to 20 °C and the vessel was charged with 229.5 mL of distilled toluene, 9.5 mL (0.071 mol) of methylacrylate, and followed 1 mL (10 wt% in toluene = 1.7 x10 $^{-3}$ mol) of methylaluminoxane as solution. The reactor then pressured was to 38 psi (2.0 bar) of ethylene and saturated for about 10 minutes. A 10 mg (1.9 x 10 $^{-6}$ mole) of catalyst and 11 mL (0.018 mol) of MAO solution was mixed and prepared for 30 minutes prior the experiment. 10 mL of the mixed catalyst solution was prepared above then introduced to the reactor via syringe. After 20 minutes, adding ethyl alcohol terminated polymerization and the polymer was collected by filtration. After stirring with diluted hydrochloric acid over night and filtering the polymer and dried in oven at 70 °C and 1.48g of product was obtained.

We polymerized ethylene with both iron(II) and iron(III) based catalysts and we picked the iron(III) based catalyst for the ethylene / 1-hexene copolymer and the iron(II) complex for the ethylene / methylacrylate copolymer. The iron(II) based catalyst would have been too active for ethylene and 1-hexene at its copolymerization would have been uncontrollable, whereas it was useful for the methylacrylate.

It had been reported in the literature that the iron(II) catalysts was more active than the iron(III) catalysts in polymerization of ethylene. The reason that the iron(III) based catalyst is less active is due to the number of electron in the d orbitals. There are 17 electrons in the coordination for iron(III) based catalyst while the iron(II) based catalyst has only 16 electrons in it coordination, making the later catalyst more reactive.

C.1. Gas Permeable Chromatography (GPC)

The analysis was carried out on a Waters Alliance GPCV 2000 high temperature instrument at Dow Chemical Company.

Sample Preparation: 15 mg of the sample was dissolved in 13 mL of TCB containing 300 ppm w/w lonol. The solutions were skaken at 160 ^{o}C for two hours. The hot solutions were filtered using a 0.5 micron stainless steel filter.

Calibration: A polystyrene/polyethylene universal calibration was carried out using narrow molecular weight distribution polystyrene standards.

C.2. Infrared Spectroscopy

Infrared spectroscopy was used to determine the copolymer composition. The Biorad Excalibur Series FTS 3000 was used to analyze the copolymers. Samples were heated between aluminum foils at 120 ^{o}C and at a pressure of 2000 psi using a Carver laboratory press machine. The thin films then were placed in the spectrometer and scanned over a wavelength range 4500 to 600 cm^{-1}.

C.3. Thermo Gravimetric Analysis (TGA)

TGA measures weight changes with temperature providing information about composition analysis and thermal stability. The procedure was carried out using a TA Instruments TGA 2050. The copolymers were heated from 50 ^{o}C to 700 ^{o}C at a rate of 10 ^{o}C / minute under nitrogen gas.

C.4. Differential Scanning Calorimetry (DSC)

DSC is a characterization technique to obtain the melting and crystallization data for polymers. The DSC 2010 by TA Instruments was used to analyze the copolymers. The samples for the DSC were prepared in the following method. About 10 mg of the solid copolymer placed in a hermetic aluminum pan. The pan was sealed with an aluminum cover. A reference pan was made with the aluminum without any sample in the pan. These two pans then were placed into the furnace in the DSC and closed the furnace. A nitrogen flow of 80 mL per second was maintained in the DSC chamber. The DSC runs were carried out at two different cooling temperatures rates: 10 ^{o}C / min and 20 ^{o}C / min. The latter heating rate was used for the first cycle to eliminate the thermal history of the polymers. The copolymers were analyzed in the temperature range between –120 ^{o}C to 250 ^{o}C.

Results and Discussion

1. Catalysts synthesis:

The following table shows the results we obtained from the elemental analysis of our catalyst compounds by Oneida Research Services.

Table 3. Elemental Analysis of $FeCl_2$ and $FeCl_3$ based catalysts:

Element	Theoretical $FeCl_2$	Experiment $FeCl_2$	Theoretical $FeCl_3$	Experiment $FeCl_3$
Hydrogen	5.9 %	5.9 %	5.5 %	4.9 %
Carbon	61.8 %	57.8 %	57.9 %	57.1 %
Chloride	13.6 %	13.8 %	19.0 %	n.d
Nitrogen	8.0 %	6.6 %	7.5 %	8.3 %

n.d: not determined

The values in Table 3 for the $FeCl_2$ and $FeCl_3$ based catalysts show good agreement between experimental and the theoretical values. These catalysts turned out to be good polymerization catalysts for polyethylene, ethylene/methylacrylate, and ethylene/1-hexene copolymers.

Table 4. Elemental Analysis of $RuCl_3$ based catalysts.

Element	Theoretical $RuCl_3$	Experiment $RuCl_3$
Hydrogen	5.1 %	0.4 %
Carbon	53.5 %	2.5 %
Chloride	17.6 %	35.5 %
Nitrogen	6.9 %	0.5 %

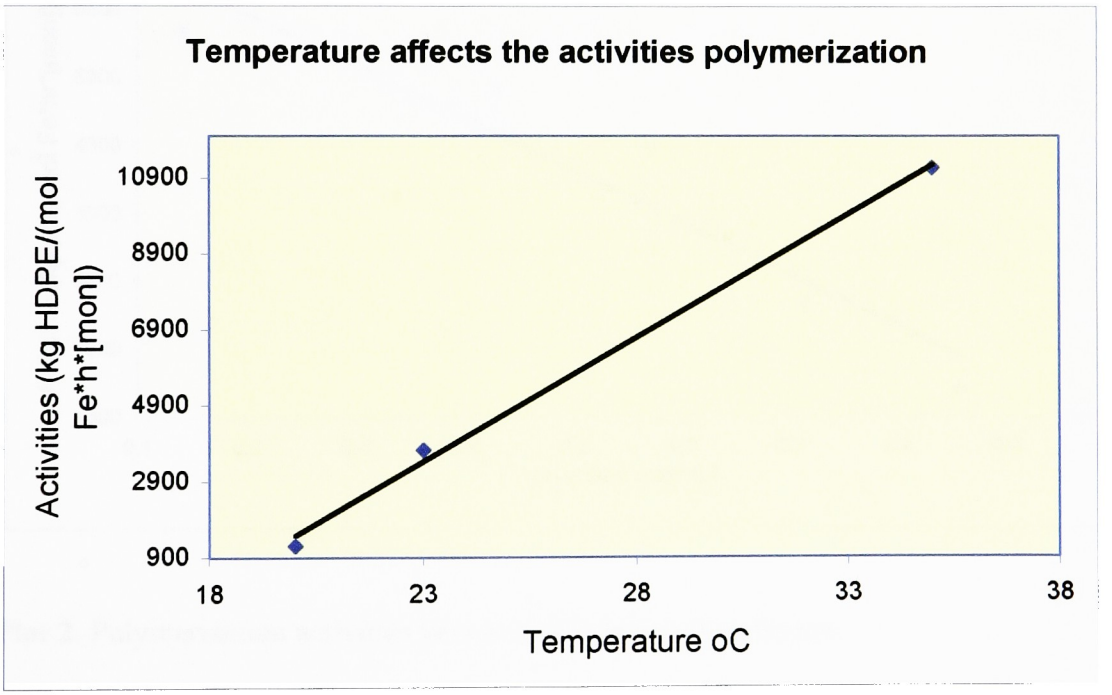
The hydrogen, carbon and nitrogen percent experimental values of $RuCl_3$ based catalyst in Table 4 do not match the theoretical values while the chloride percent values just about double. This indicates that the ruthenium did not react well with the diimine ligand and the desired catalyst was not formed. Consequently, the producted catalyst was not active for polymerization of ethylene.

2. Polymerizations

Table 5. Ethylene polymerization runs with $FeCl_3$ based catalyst.

Exp. No.	Ethylene mol / L	Temperature °C	Poly. time minute	Activity (kg HDPE /(mol Fe h [mon])	Yield g
PE.1	0.285	20	25	1213	1.44
PE.2	0.285	23	20	3716	3.54
PE.3	0.285	35	8	11158	4.24

The activities values in Table 5 were based on the yield obtained from the final product of polymers during filtering and drying in the oven over night. As one can see in the Plot 1 the activities increased as the temperature was increased.



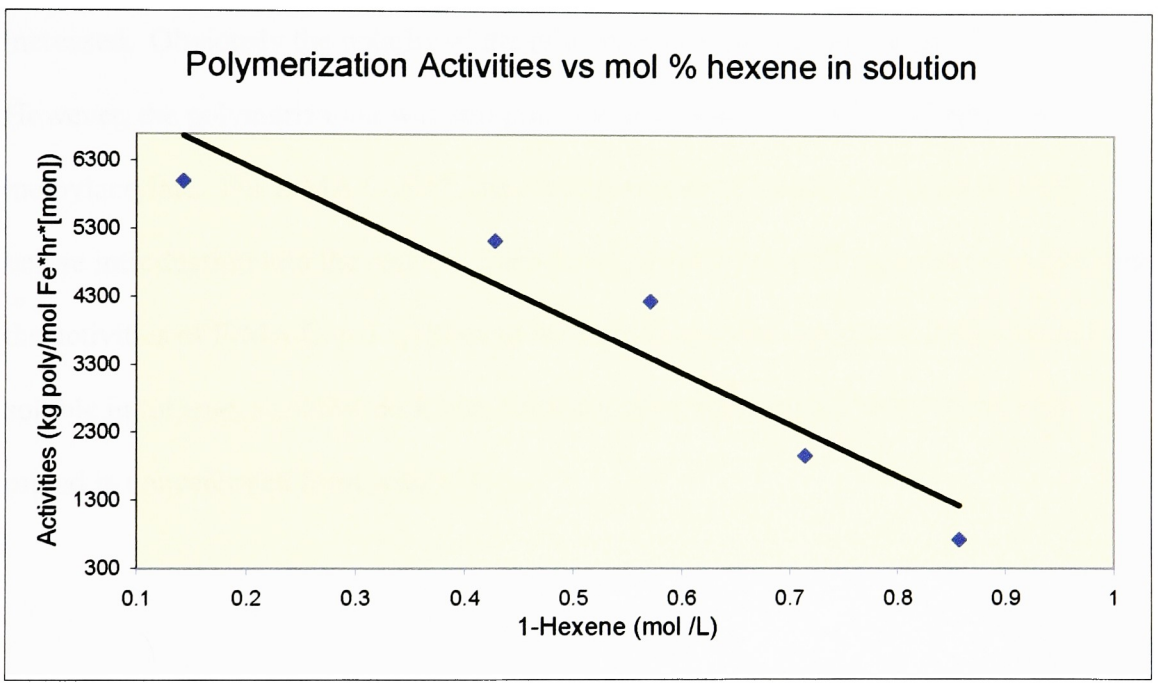
Plot 1. Temperature affects the activities of polymerization.

Table 6. Ethylene/1-hexene copolymerization runs with $FeCl_3$ based catalyst.

Exp. No.	1-hexene mol / L	Temperature °C	Poly. time minute	Activity (kg E/H Cop /(mol Fe h [mon])	Yield g
E/H Cop 1	0.143	25	7	6008	3.00
E/H Cop 2	0.428	18	6	5133	3.66
E/H Cop 3	0.571	18	7	4246	4.24
E/H Cop 4	0.714	18	5	1970	1.64
E/H Cop 5	0.857	18	15	725	2.07

Ethylene = 0.285 mol/L, MAO = 1.7×10^{-3} mol.

As indicated in Plot 2, the 1-hexene monomer varies affected the activities during polymerization. As the amount of monomer used increased the activities get lower.



Plot 2. Polymerization activities versus mol % hexene in solution.

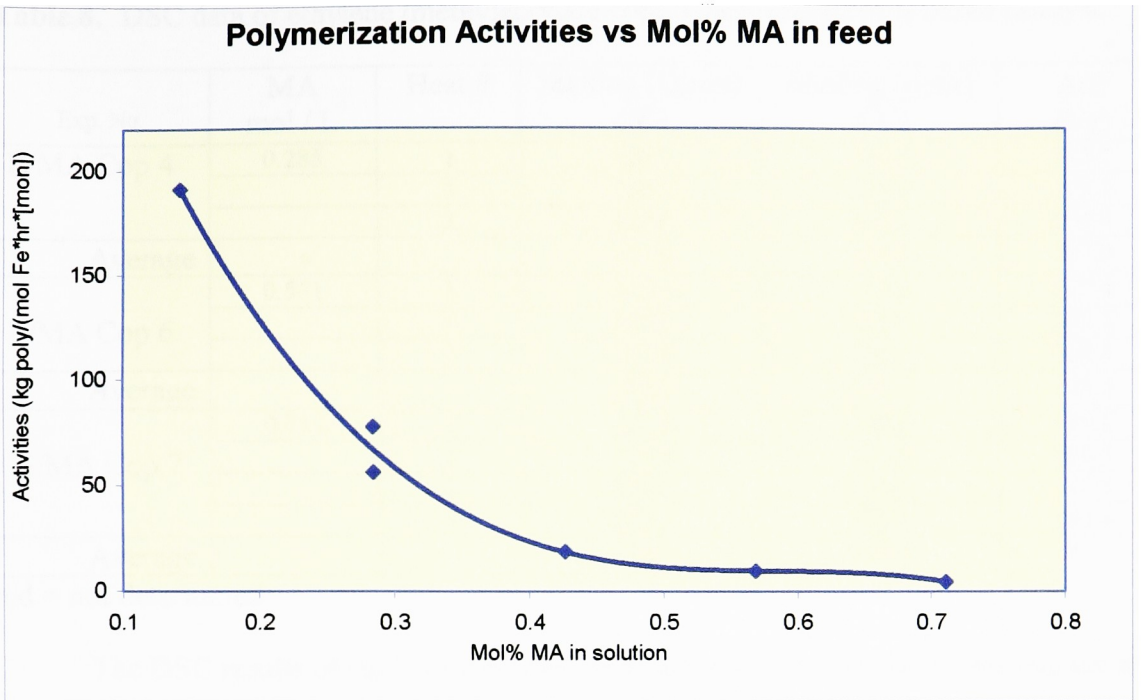
We also attempted to copolymerize 5-hexene-1-ol with ethylene. However, absolutely no activities could be observed even at the lowest concentrations of this polar comonomer (0.143 mol / L). With one test we started polymerization with pure ethylene and the addition of 5-hexene-1-ol essentially quenched the system.

Table 7. Polymerization runs with $FeCl_2$ based catalyst.

Exp. No.	methylacrylate mol / L	Poly. Time minute	Activity (kg polymer / (mole Fe h [mon]))	Yield g
E/MA Cop 2	0.142	15	191	2.04
E/MA Cop 3	0.284	20	56	1.07
E/MA Cop 4*	0.284	20	78	1.48
E/MA Cop 5	0.426	35	19	0.78
E/MA Cop 6	0.569	35	10	0.48
E/MA Cop 7	0.711	50	5	0.38

*premixed, 11mL MAO 10% (3.3×10^{-2} mol /L)
Ethylene = 2.0 bar (0.285 mol / L), and Temperature = 20 °C

The yields and activities decreased as the methylacrylate monomer concentration increased. Obviously the polarity of the monomer still had a deactivating effect. However, the polymerization was still proceeding at relatively high concentration of methylacrylate. For E/MA Cop 4*, the catalyst was mixed with co-catalyst (MAO) before introduction into the reactor. The activity of E/MA Cop 4* was clearly higher than the activities of E/MA Cop 3. Although the transition metal compound itself was not soluble in toluene, a soluble dark blue color complex was formed when the catalyst mixed in concentrated form with MAO.



Plot 3. Polymerization activities versus mol % of methylacrylate in feed.

This diagram indicates that the activities tend to decrease as more amount of methylacrylate monomer is increased in the reaction.

Table 8. DSC data of ethylene /methylacrylate copolymers using $FeCl_2$ based catalyst.

Exp. No.	MA mol / L	Heat #	Melting (Onset) (°C)	Melting (peak) (°C)	ΔHf (J/g)
E/MA Cop 4	0.285	1	126.9	136.5	215.2
		2	128.0	136.8	203.1
		3	128.0	136.5	205.4
Average			127.6	136.6	207.9
E/MA Cop 6	0.571	1	125.4	132.2	227.9
		2	124.6	131.5	199.5
		3	124.7	131.4	188.6
Average			124.9	131.7	205.3
E/MA Cop 7	0.714	1	123.5	130.0	229.2
		2	124.8	130.5	210.9
		3	124.5	130.6	210.1
		4	123.4	129.6	194.4
Average			124.3	130.2	211.2

n.d = not determined

The DSC results of selected ethylene/methylacrylate copolymers shows that the melting point decreases slightly with increasing concentration of methyl acrylate contents. These DSC experiments were run at temperatures from –120 °C to 250 °C, heating rate at 10 °C per minute, and the flow rate at 50 cc per minute. No glass transition could be observed from all the samples scans. Immediately after the third heat, the melted E/MA Cop 7 was removed from the hot DSC, and placed directly into liquid nitrogen in an attempt to freeze the sample in the amorphous state. This was done to induce the appearance of a possible Tg during the fourth heat. When the DSC itself had been cooled to about 15 °C, the quick-quenched sample was placed back into the DSC. The instrument and sample were then cooled to –110 °C prior to the fourth heat and stilled there was not any apparent of Tg peak appear. The melting temperature decreases slightly as the amount of monomer is increased. The melting temperatures, however, are not sharply lower than that of pure polyethylene (HDPE) indicating that the copolymers are highly crystalline and only low amounts of methylacrylate have been incorporated. The ΔH of copolymers was decreased as the copolymers recrystallized for second heated and third heated.

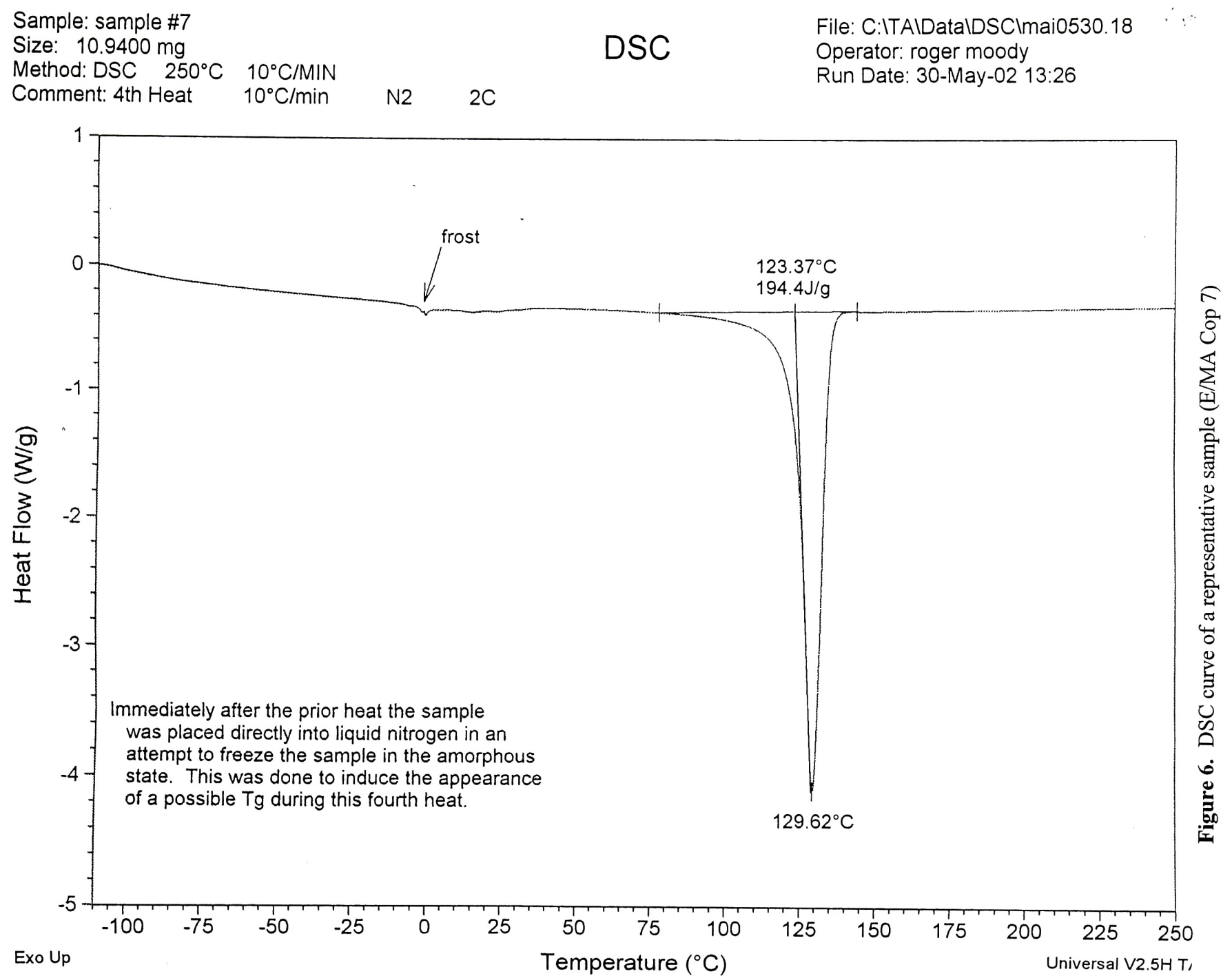


Figure 6. DSC curve of a representative sample (E/MA Cop 7)

GPC Analysis results:

Table 9. GPC results of copolymers using $FeCl_2$ based catalyst.

Exp. No.	Ethylene mol / L	Methylacrylate mol / L	Mp	Mn	Mw	Mz	Mw / Mn
E/MA Cop 3	0.285	0.284	36,400	20,700	39,400	60,400	1.90
E/MA Cop 4*	0.285	0.284	28,100	15,500	28,700	43,200	1.84
E/MA Cop 5	0.285	0.426	22,000	11,800	22,800	34,600	1.93
E/MA Cop 6	0.285	0.569	18,600	10,200	20,200	31,100	1.97
E/MA Cop 7	0.285	0.711	15,700	7,900	15,800	23,700	1.98

The gel permeable chromatography results in Table 9 show the molecular weight decreases as the methylacrylate concentration is increased. The distribution is narrow and this is an indication that the catalyst still forms predominantly one type of active site. The Figure 6 (E/MA Cop 3) below shows the typical unimodal shape found for all copolymers (for more diagrams see the Appendix). This is an indication that the active catalyst is indeed a single-site catalyst in contrast to heterogeneous titanium catalyst that cause broader molecular weight distributions, e.g. $Mw / Mn \approx 10$.

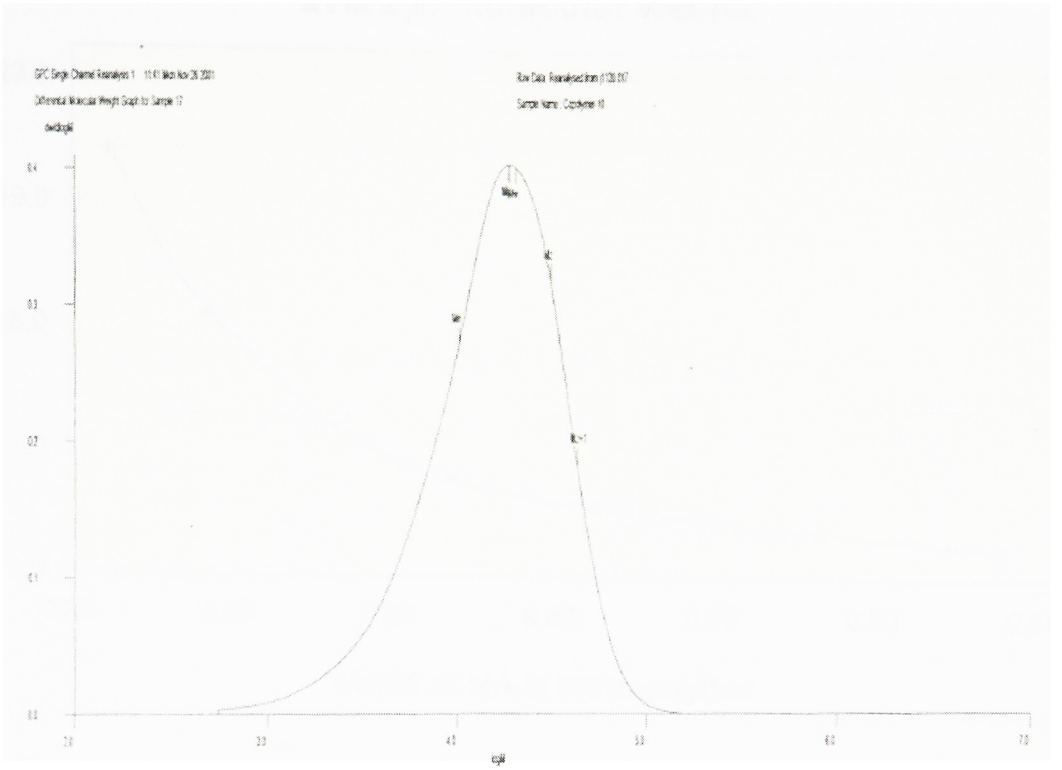
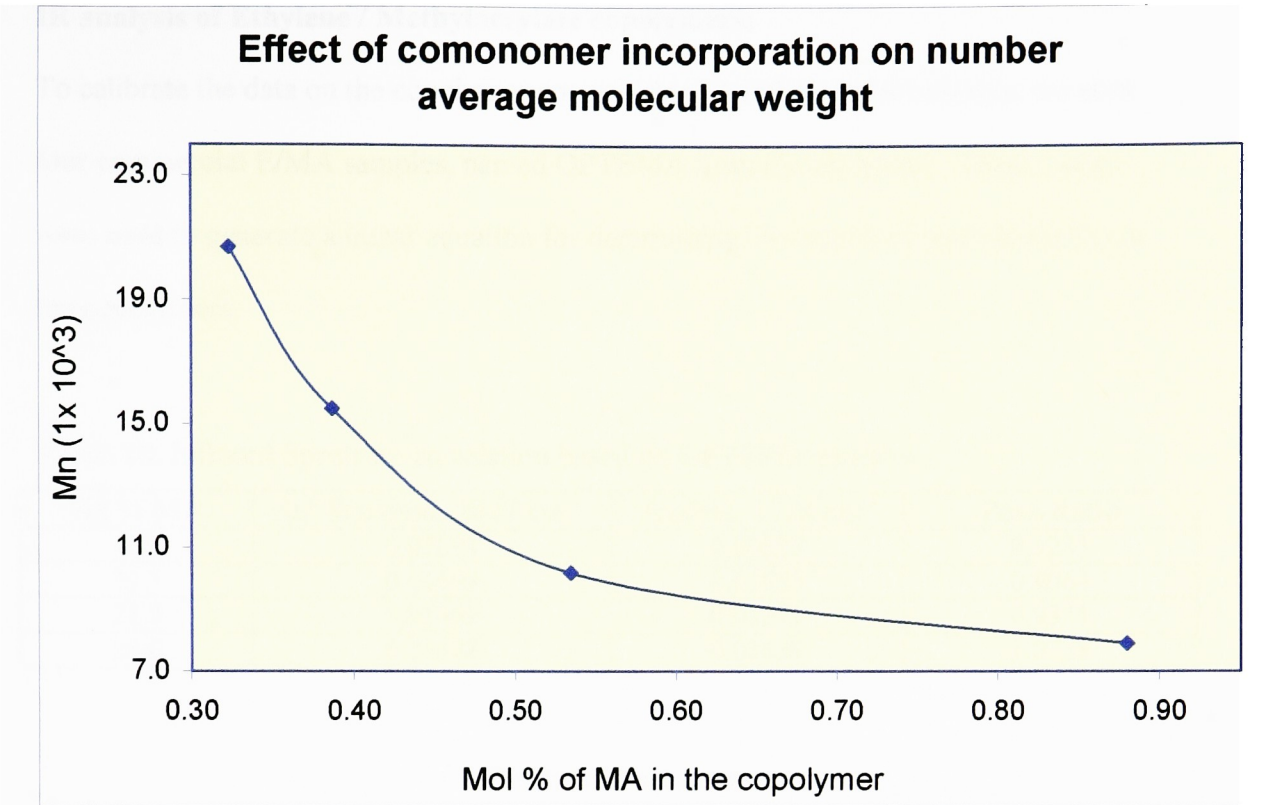


Figure 6. GPC curve of a representative sample (E/MA Cop 3)



Plot 4. The number average molecular weight versus mol % of methylacrylate in the copolymer.

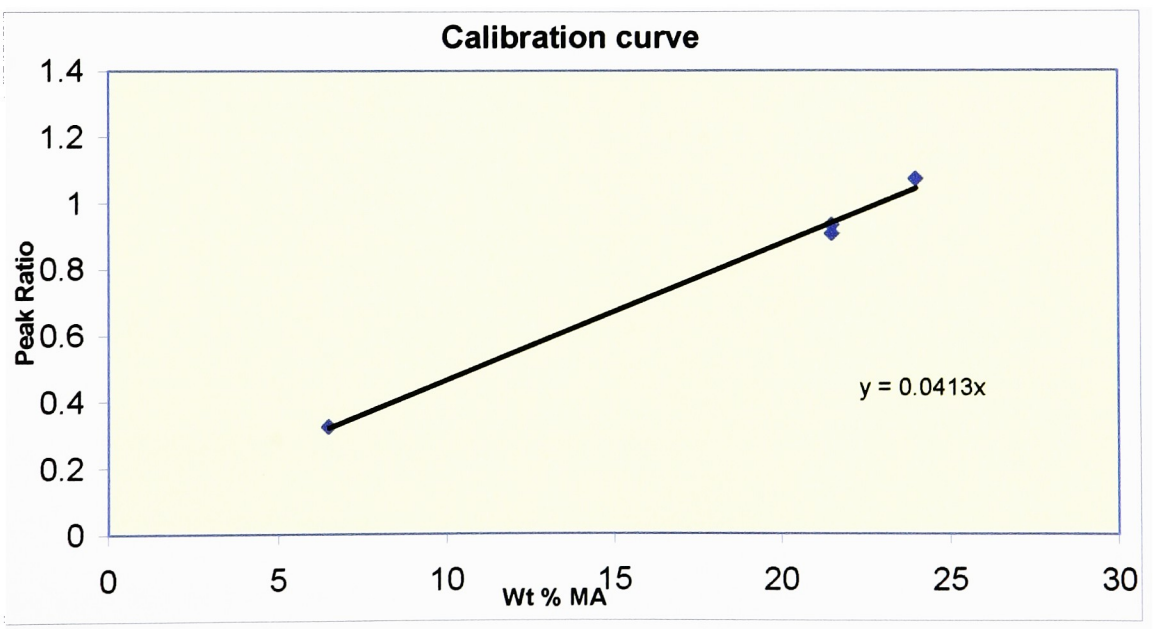
As the amount of methylacrylate concentration in the solution is increased, the average molecular weight is lowered.

IR analysis of Ethylene / Methylacrylate copolymers:

To calibrate the data on the copolymer composition by infrared spectroscopy, we used four commercial E/MA samples, named OPTEMA from Exxon Mobil. These values were used to generate a linear equation for determining the mol % of methylacrylate in the copolymers.

Table 10. Infrared Spectrum correlation based on OPTEMA samples.

Wt % MA	Int Standard, 2847 cm^{-1}	Analyte, 1738 cm^{-1}	Peak Ratio
6.5	0.02094	0.00677	0.3233
21.5	0.01693	0.01535	0.9064
21.5	0.01469	0.01371	0.9331
24.0	0.01528	0.01639	1.0728



Plot 5. Calibration curve using IR results of copolymers obtained from Exxon Mobil.

First column, weight % of methylacrylate in the copolymers that obtained from Exxon Mobil and the second column values were obtained from Infrared spectroscopy by using

standard peak at 2847 cm^{-1} of CH_3 stretched. The third column, values were analyzed using C=O peak at 1738 cm^{-1} and the values of the final column were the ratios of the two.

An equation was used from the calibration curve generated to give weight % in our copolymers. E/MA Cop 7 gave the highest amount of methylacrylate in the copolymer.

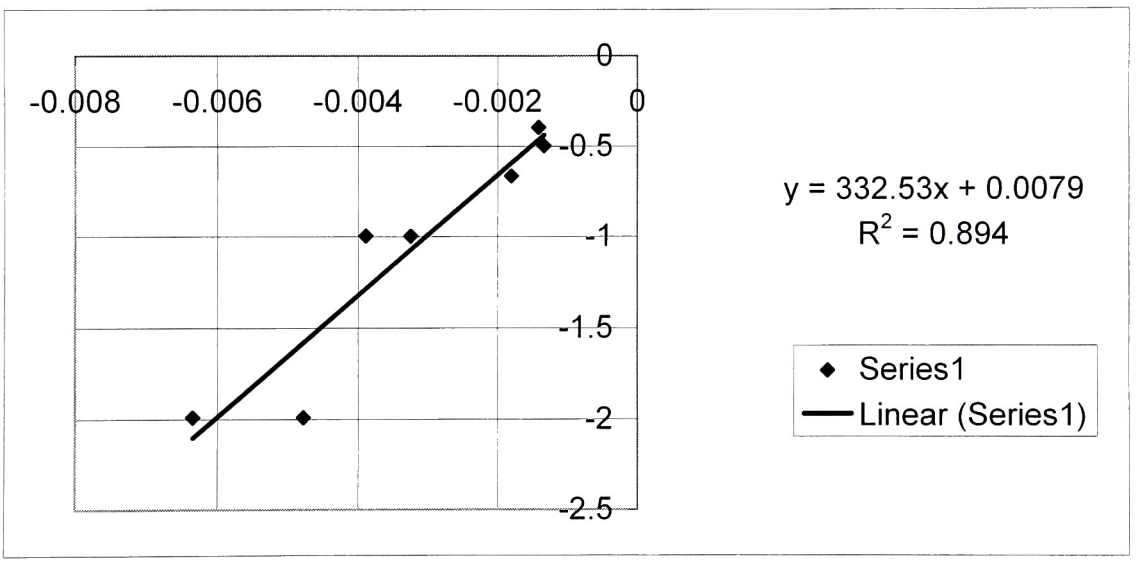
Table 11. Mol % of methylacrylate in the copolymers obtained from IR based on Plot 5.

Experimental Number	Mol % of MA	Wt % of MA in copolymers
E/MA Cop 2	0.12	0.37
E/MA Cop 3	0.32	0.99
E/MA Cop 4	0.39	1.18
E/MA Cop 5	0.40	1.23
E/MA Cop 6	0.53	1.62
E/MA Cop 7	0.90	2.65

Determination of reactivity ratio for ethylene / methylacrylate copolymers:

Table 12. Data generated from Fineman-Ross based on Equation on page 20.

Experiment No.	MA mol / L	f1	F1	X	Y
E/MA Cop 1	0.143	0.666	0.998	- 0.00635	- 1.989
E/MA Cop 2	0.143	0.666	0.999	- 0.00478	- 1.991
E/MA Cop 3	0.284	0.500	0.997	- 0.00324	- 0.00142
E/MA Cop 4*	0.284	0.500	0.996	- 0.00339	- 0.9968
E/MA Cop 5	0.426	0.399	0.996	- 0.00180	- 0.9961
E/MA Cop 6	0.569	0.333	0.995	- 0.00134	- 0.6631
E/MA Cop 7	0.711	0.285	0.991	- 0.00142	- 0.3956



Plot 6. Fineman-Ross plot for E/MA copolymerizations

The reactivity ratios of r_1 and r_2 values are and 332 and 0.0079 respectively. This would indicates that the copolymerization leads essentially to a random monomer sequence distribution with a slightly tendency to block formation since $r_1 \times r_2$ is 2.7. The polymerization of ethylene is favored by several orders of magnitude over that of methylacrylate.

H-NMR analysis:

By estimation on the H-NMR analysis, we obtained close to 3.0 mol % for the experiment with the highest methylacrylate fed in the reaction. However, the IR spectroscopy of our copolymer have more reliability, and it copolymer with the highest methylacrylate content (E/MA Cop 7) contains close to 1 mol % of methylacrylate.

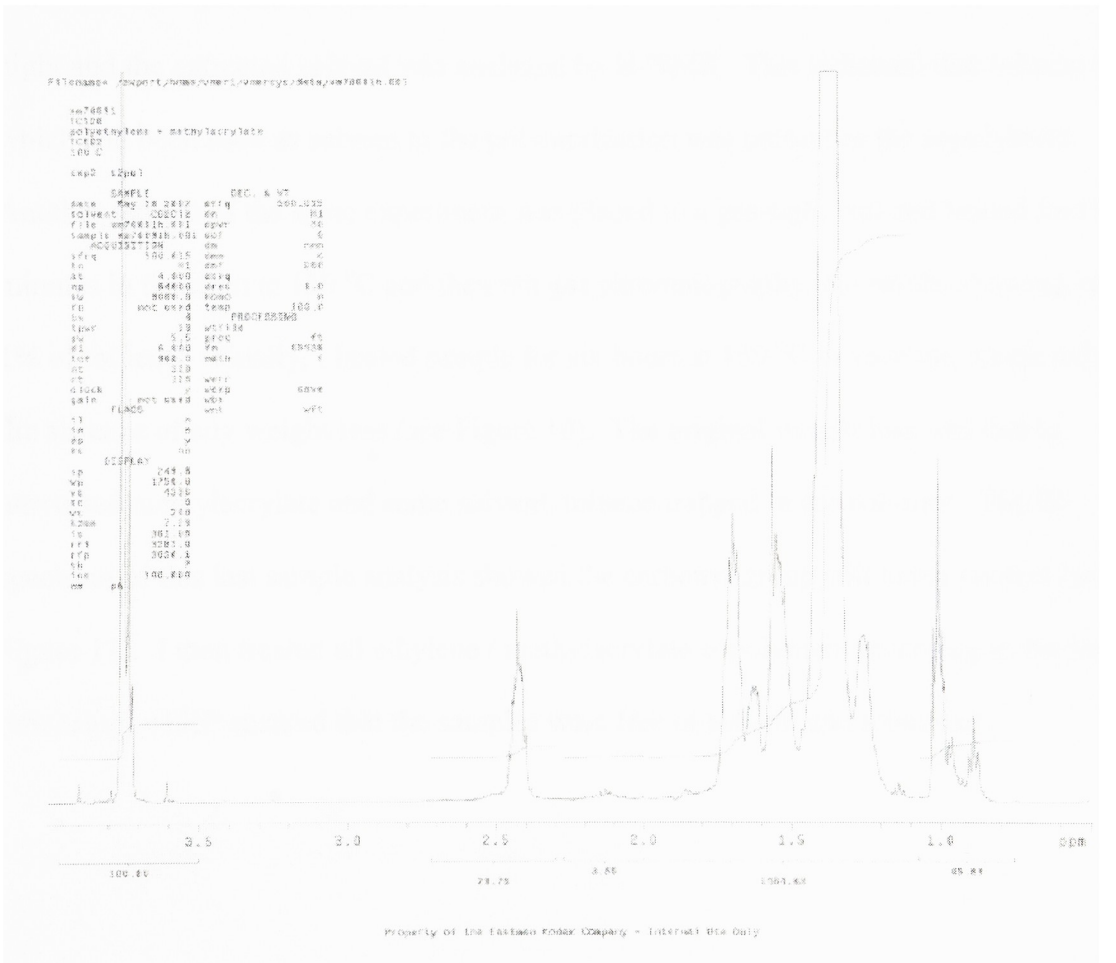


Figure 7. H-NMR spectrum of copolymer (E/MA Cop 5).

In the H-NMR spectrum, the CH_3 group of the methylacrylate originates the peaks at 3.8 ppm. The next peaks at 1.4 and 1.6 ppm are originates to CH_2CH_2, and CH_2CH_2 of methylacrylate and ethylene respectively.

Initial issues with nonpolymeric residues in E/MA copolymers - TGA, e.g.

The TGA results showed original weight loss for ethylene / methylacrylate copolymers in Figure 8. These copolymers then were further characterized. To find out what carried this weight loss I had to perform several methods. To resolve this issue, I heated the copolymers for two hours at 160 ^{o}C under argon. However, there still was a weight loss as determined by TGA in Figure 9. Next, I soaked the samples with deuterated THF over night and the extracted solvent was analyzed by H-NMR. This indicated that toluene still which had been used as solvent in the polymerization was present in the copolymers. Another sample of the same experiment was placed in a gas-tight vial and heated for15 minutes in the oven at 130 ^{o}C and then ran gas chromatography, the results showing only 1% of toluene. Finally, I heated sample for six hours at 160 ^{o}C in vacuum, which led to the absence of any weight loss (see Figure 10). The original weight loss was due to unreacted methylacrylate and some solvent, toluene trapped in the polymer. The IR spectrum of this last sample analysis showed the carbonyl group still being present (see Figure 11). I then treated all ethylene / methylacrylate copolymers according to the last procedure, which ensured that the samples were free of solvent and monomer.

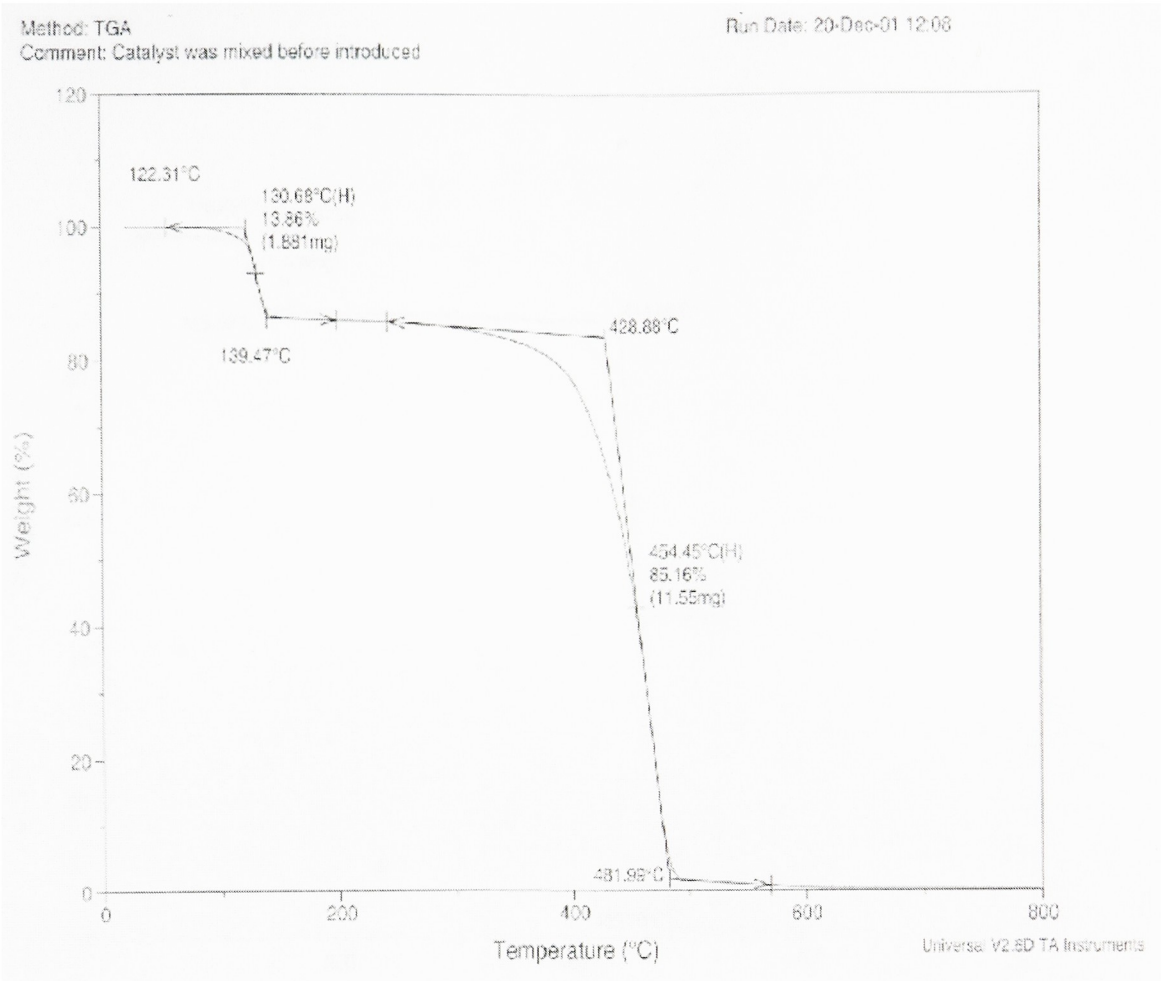


Figure 8. TGA of copolymer (E/MA Cop 4) sample was dried in oven at 70 ^{o}C over night.

Figure 8 was obtained from TGA analyzed.

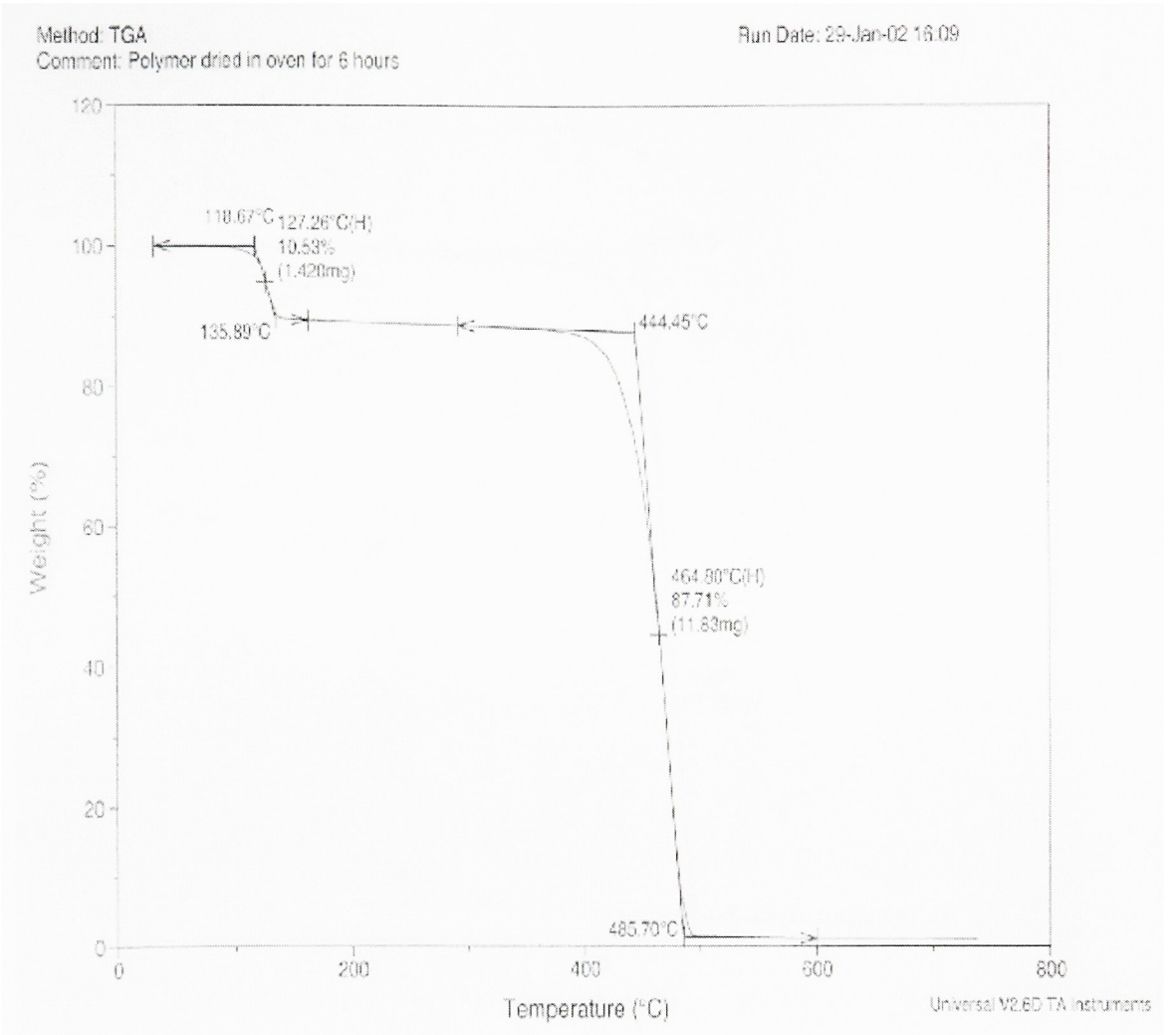


Figure 9. TGA of copolymer (E/MA Cop 4) sample was heated for two hours at 160 ^{o}C under argon.

Figure 9 also was obtained from TGA analyzed

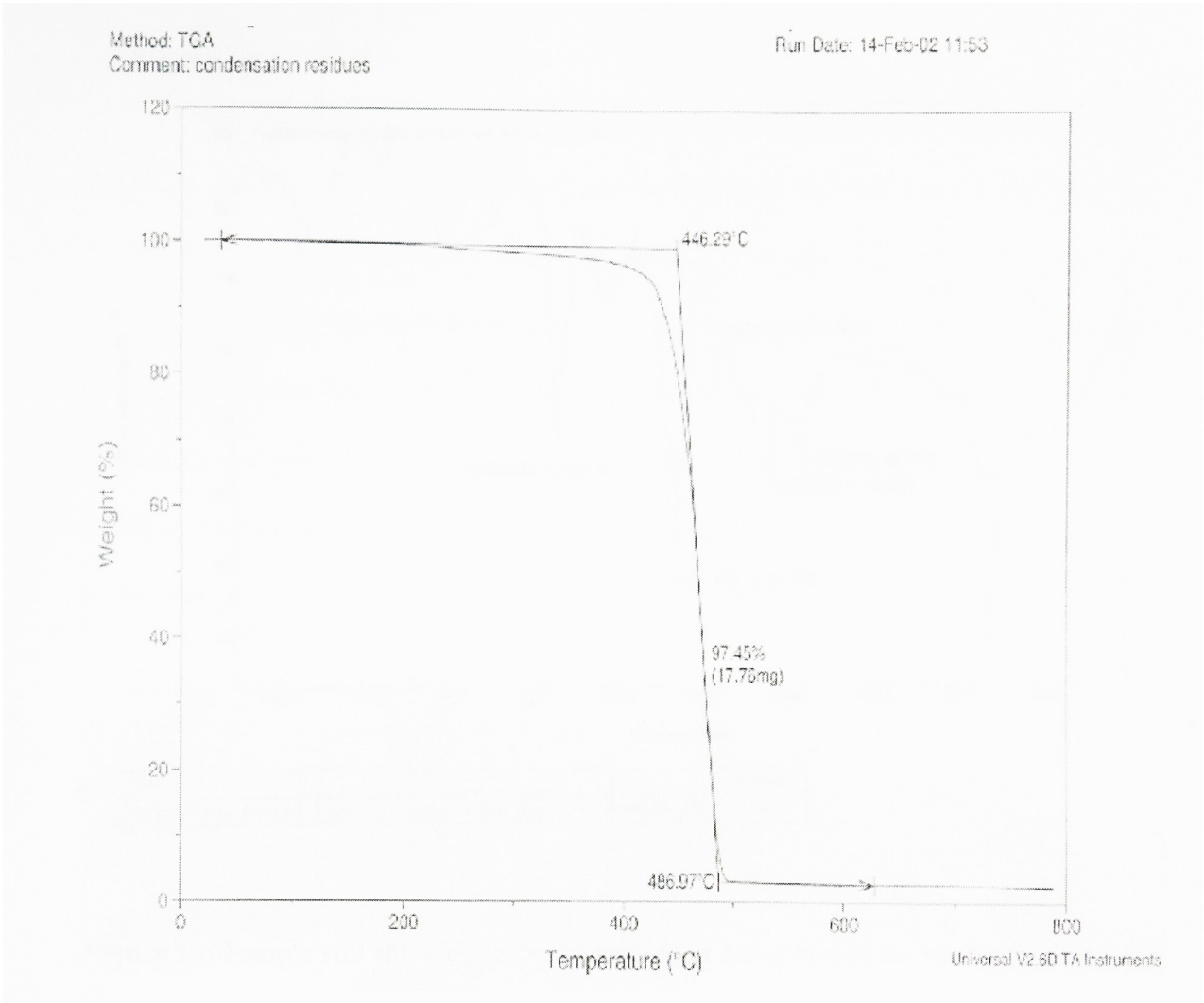


Figure 10. TGA of copolymer (E/MA Cop 4) sample was heated for six hours at 160 ^{o}C in vacuum.

Figure 10 obtained by TGA analyzed method.

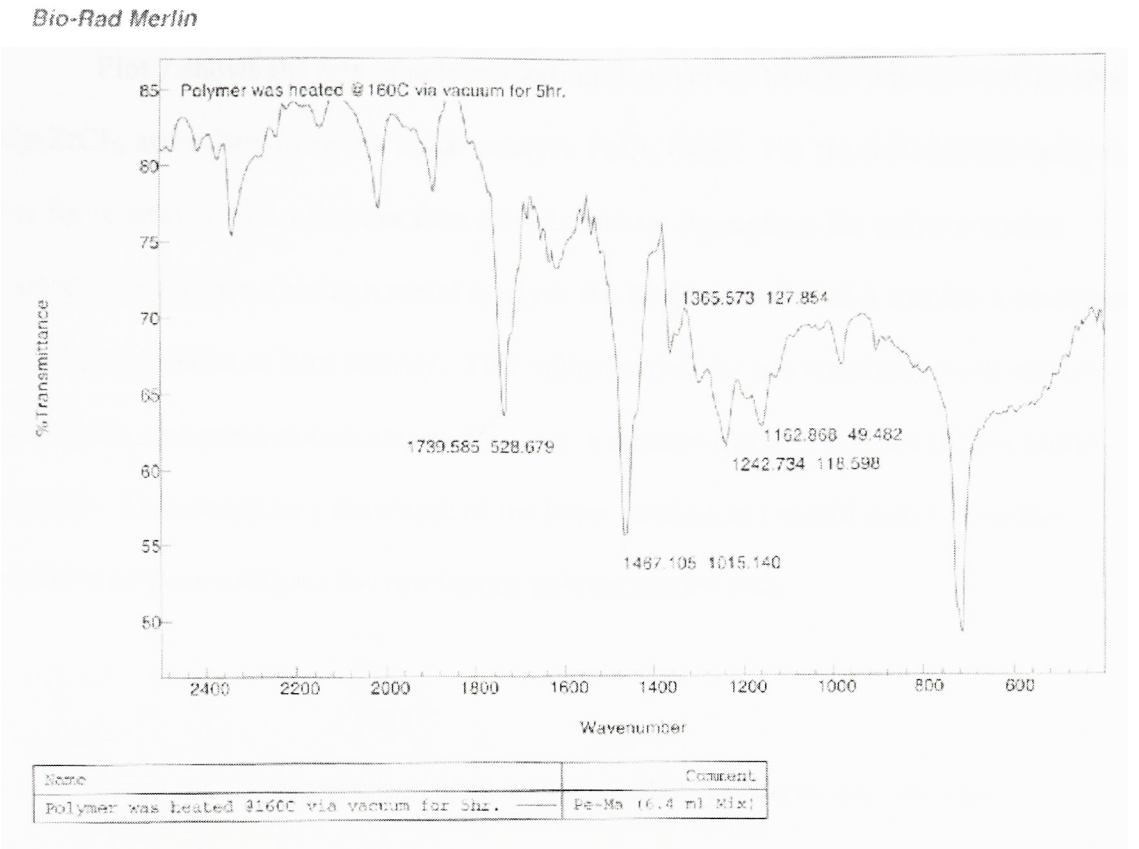
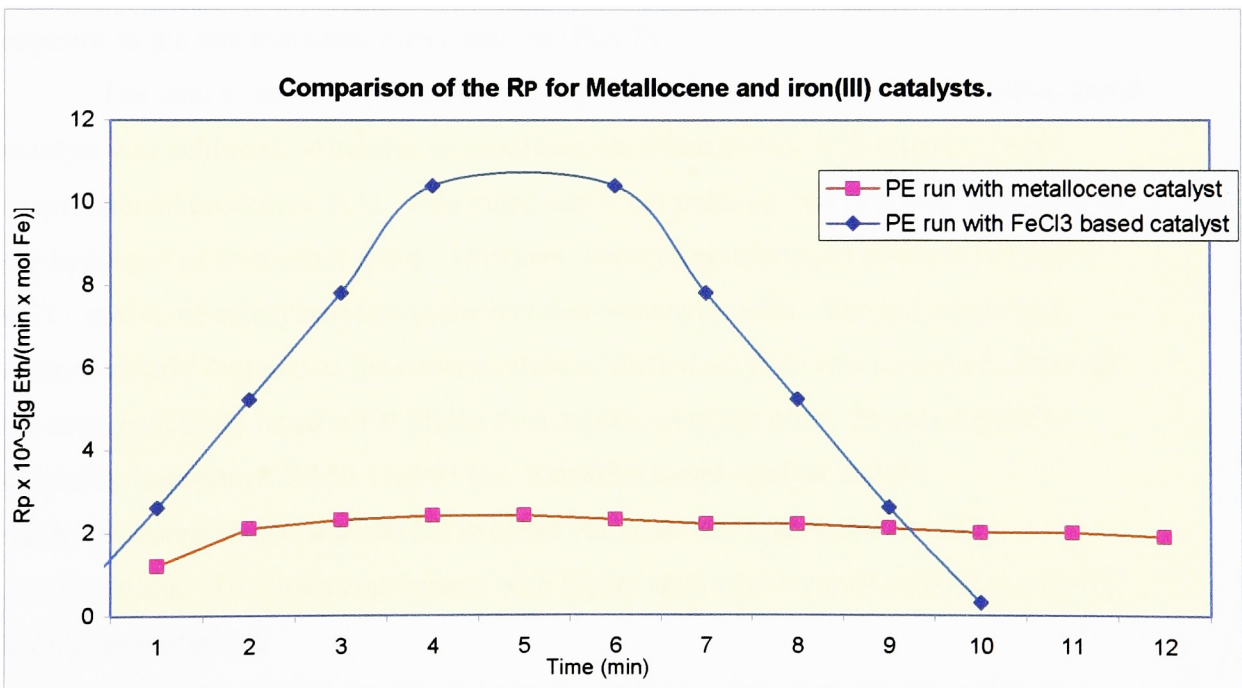


Figure 11. Sample still showing carbonyl peak after being heated for six hours at 160 ^{o}C in vacuum.

Figure 11 was obtained from Infrared spectroscopy analyzed.

Polymerization kinetics:

Plot 7 shows the rate of polymerization (Rp) versus time for metallocene catalyst, Cp_2ZrCl_3, and a late transition metal catalyst, $FeCl_3$ based. For the metallocene catalyst, the Rp reached a high value but then stayed constant throughout the polymerization period. For the late transition metal catalyst, the Rp increases until it reaches a maximum and then decreases to zero activity. This indicates that the late transition metal catalyst undergoes, and some deactivate reaction, e.g. a reduction after it reaches the maximum activity. This would be a drawback of the latter catalyst and would require repeated addition of these catalysts for continuous polymerization runs.



Plot 7. Comparison of the rate polymerization for metallocene and iron(III) catalyst.

Plot 7 was obtained using values of Rp vs time of each polyethylene runs with difference catalysts.

Conclusion

I was able to synthesize two late transition metal catalysts, which had been discovered in the last couple of years. I slightly modified the procedure of the ligand addition and obtained yields comparable to those described in the literature.

The elemental analyses of these catalysts showed in Table 3 that our syntheses led to the desired products. An attempt to produce the analog ruthenium catalyst failed showed in Table 4. There may be alternatives to synthesize the latter catalyst by using other ruthenium based metal organic compounds.

Moreover, the catalysts performed well in the polymerization with ethylene as expected to previous reports in the literature. Interestingly, our comparison with a typical metallocene catalysts showed that the late transition metal catalyst had a higher activity, however only for a limited time. In this sense, the metallocene catalyst, which has a constant activity and is a pseudo living catalyst at ambient or higher temperatures, is superior to the late transition metal catalyst (Plot 7).

The goal to produce polymers with a polar monomer with the late transition metal catalyst was achieved. Attempts to copolymerize 5-hexen-1-ol with ethylene failed (experimental procedure B.1). This monomer is too polar i.e. has to strong an acidity of the hydrogen of its alcohol group. However, copolymerizations of ethylene with up to 0.711 mol /L of methylacrylate in the reaction were successful. The polymerization activity clearly dropped as the concentration of methyl acrylate was increased, although the drop in activity taped off at higher concentrations of the ester. Premixing of the catalyst components, E/MA Cop 4* (i.e. transition metal catalyst and the methylaluminoxane cocatalyst) led to better activities and higher comonomer incorporation. To obtain copolymers with higher ester content such catalyst premixing should be performed.

The Differential Scanning Calorimetry indicates that all copolymers still are highly crystalline. The melting points for the copolymers with higher methylacrylate content are only a couple of degrees lower than that of the high-density polyethylene. This was a first indication that only a relatively small amount of methyl acrylate had been incorporated. No glass transition could be observed in any of the copolymers.

The determination of the copolymer composite mainly by FT-IR and H-NMR spectroscopy verified that the maximum amount of methyl acrylate in the copolymer was close to 1 mol %. Using all seven copolymers data in a Fineman-Ross Plot, the reactivity ratios were determined as $r_E = 315$ and $r_{MA} = 0.008$. One can conclude therefore that ethylene polymerizes much faster than the methyl acrylate and that the tendency for the methyl acrylate to homopolymerize with the given catalyst system is very low.

The GPC Plots show unimodal curves, with relatively narrow distribution. As is typical for all single-site catalysts, including metallocene catalysts, the values Mw / Mn are around 2. This may explain also further why the samples felt tough and brittle. Furthermore, the low dispersity indicates that no changes to the active catalyst species did occur in the presence of the polar monomer.

Future Work:

1. Try to polymerize a series of ethylene / methyl acrylate copolymer with iron(II) based catalyst at lower temperatures to increase the comonomer incorporation
2. Use these for polymerizing some electroconductive polymers such as polyacetylene and its derivatives.
3. Find a better method to purify the final product so there is no solvent trapped in the copolymers.
4. Find any solvent that more readily dissolves the copolymer so the characterization is more facile.

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E/MA Cop 4*

ıixed

TGA

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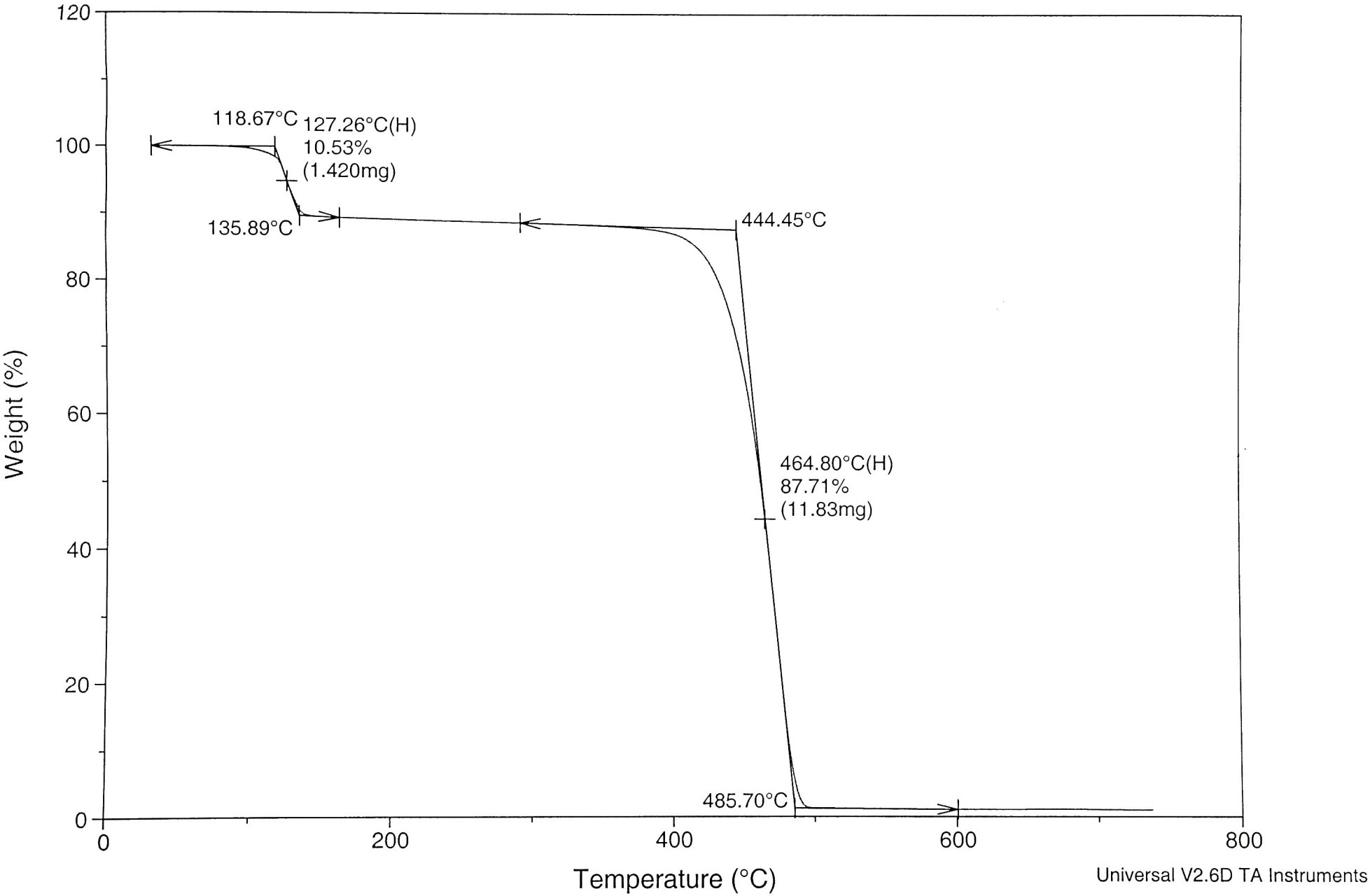
Comment: Polymer dried in oven for 6 hours



Universal V2.6D TA Instruments

E/MA Cop 4*

TGA

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Operator: Xuan Mai
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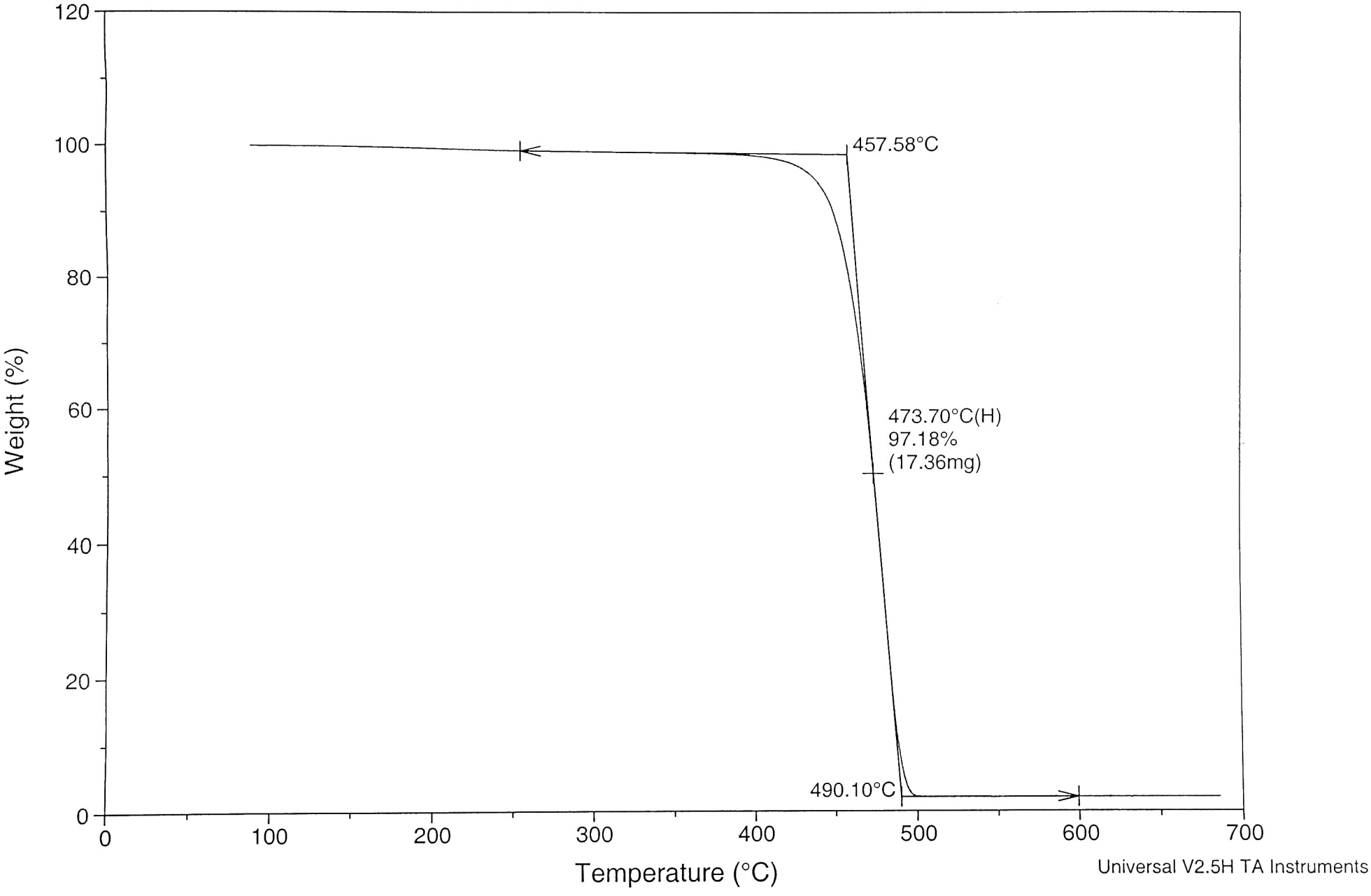
Comment: Polymer was heated at 160 C under Argon



Universal V2.5H TA Instruments

E/MA Cop 5

Method: TGA

TGA

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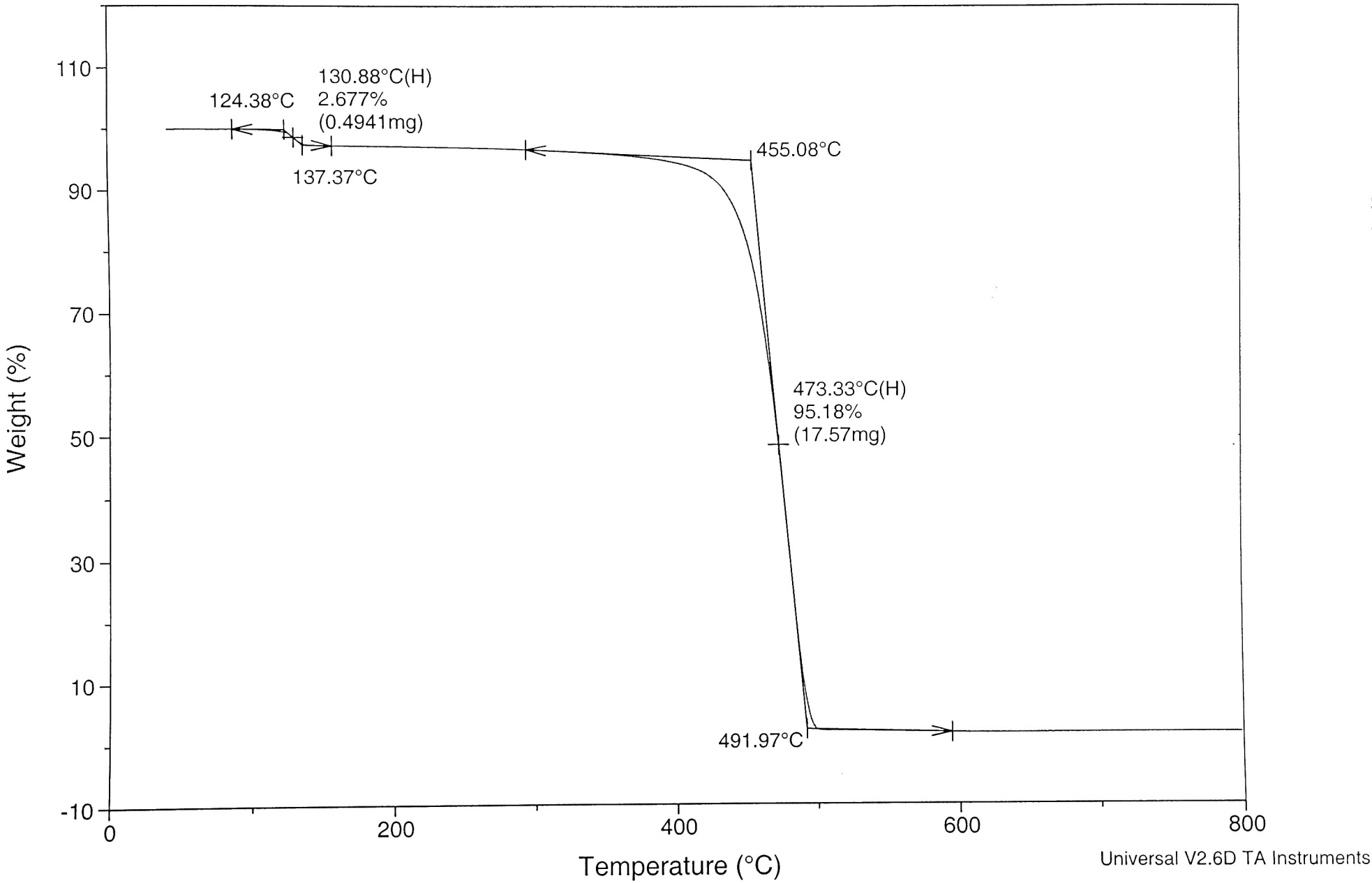

Universal V2.6D TA Instruments

E/MA Cop 6

Comment: (12.8 ml)

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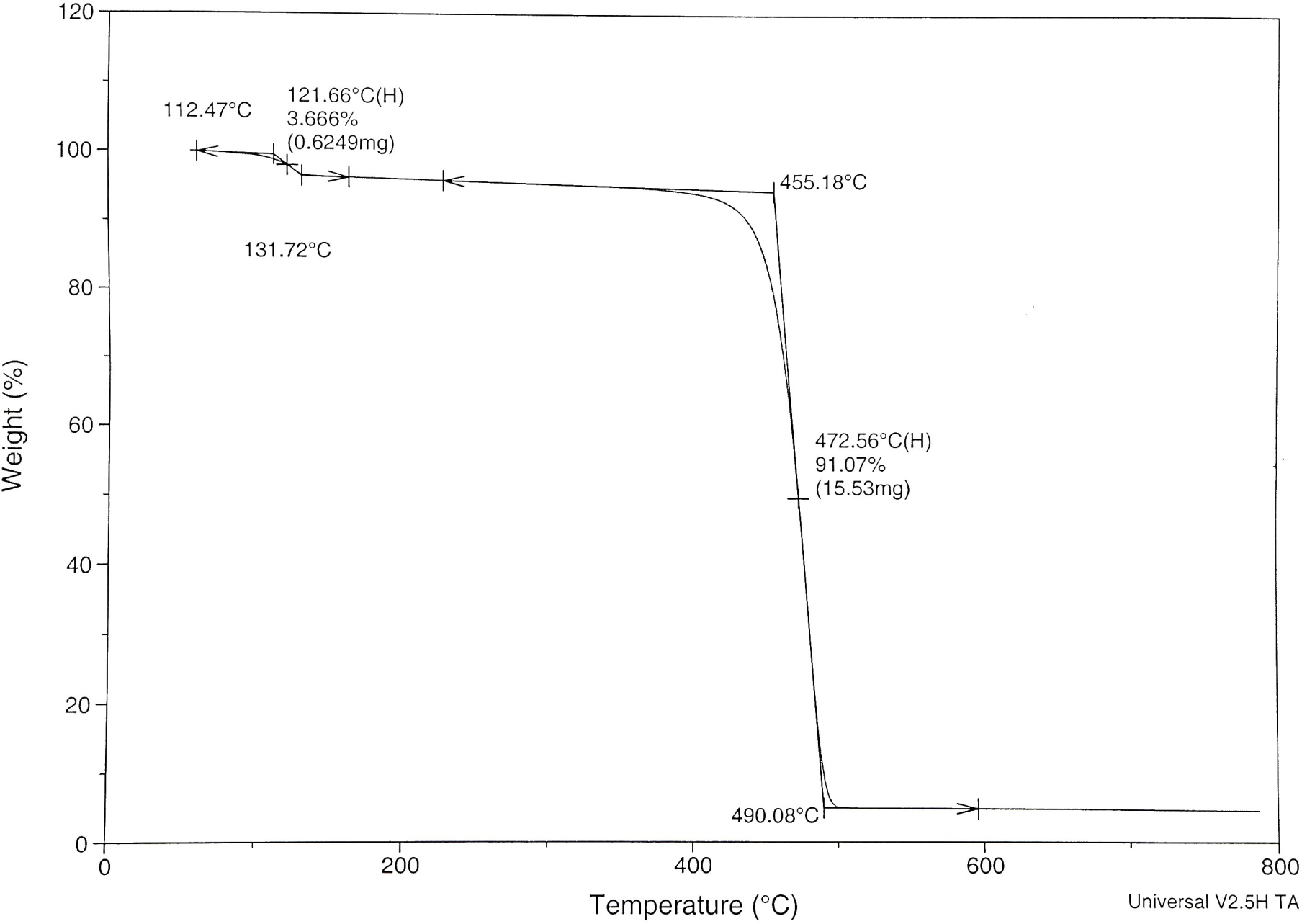

Universal V2.5H TA Instruments

E/MA Cop 7

Comment: (16 ml)

TGA

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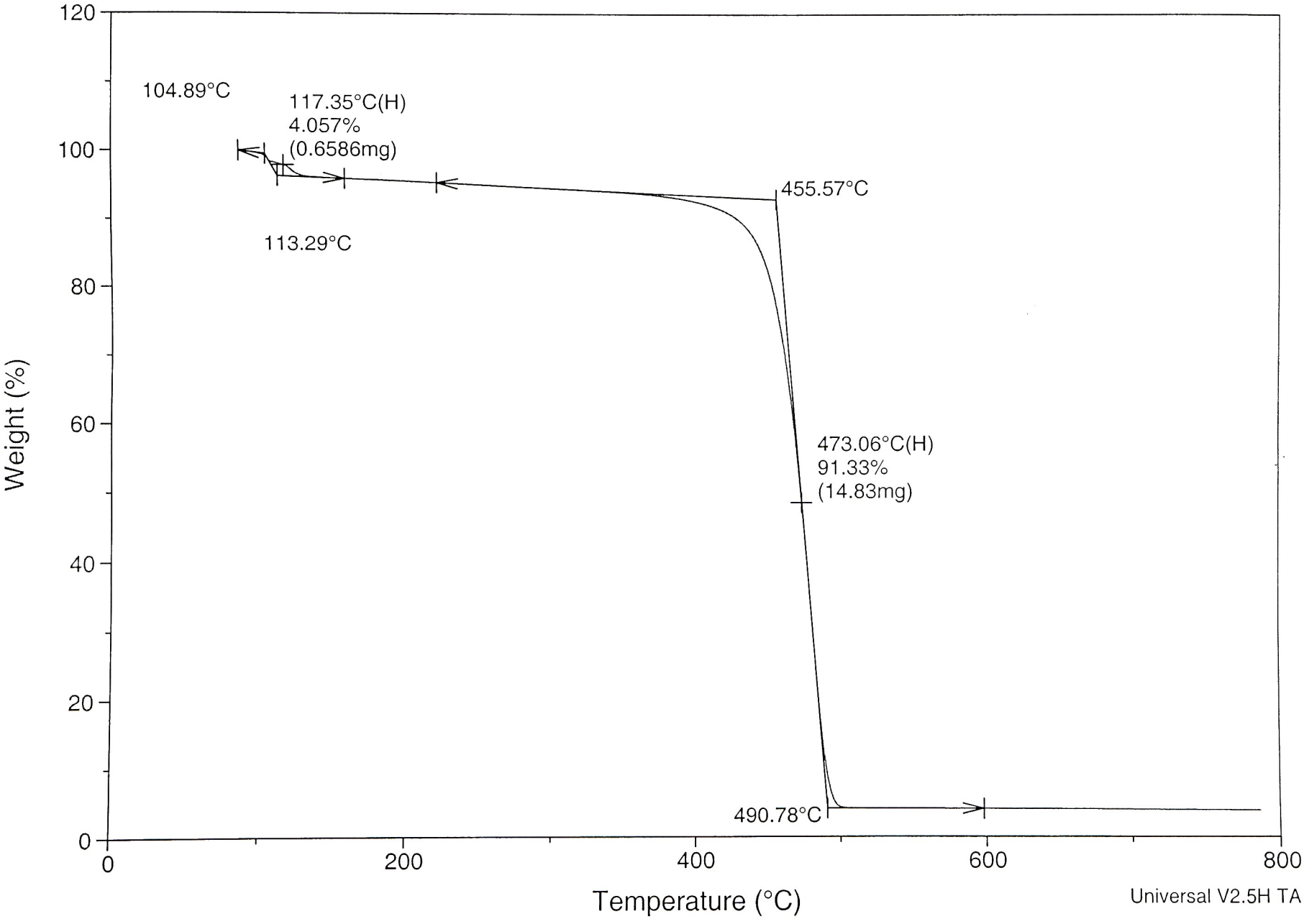
Run Date: 18-Jan-02 17:23



Universal V2.5H TA Instruments

E/MA Cop 4*

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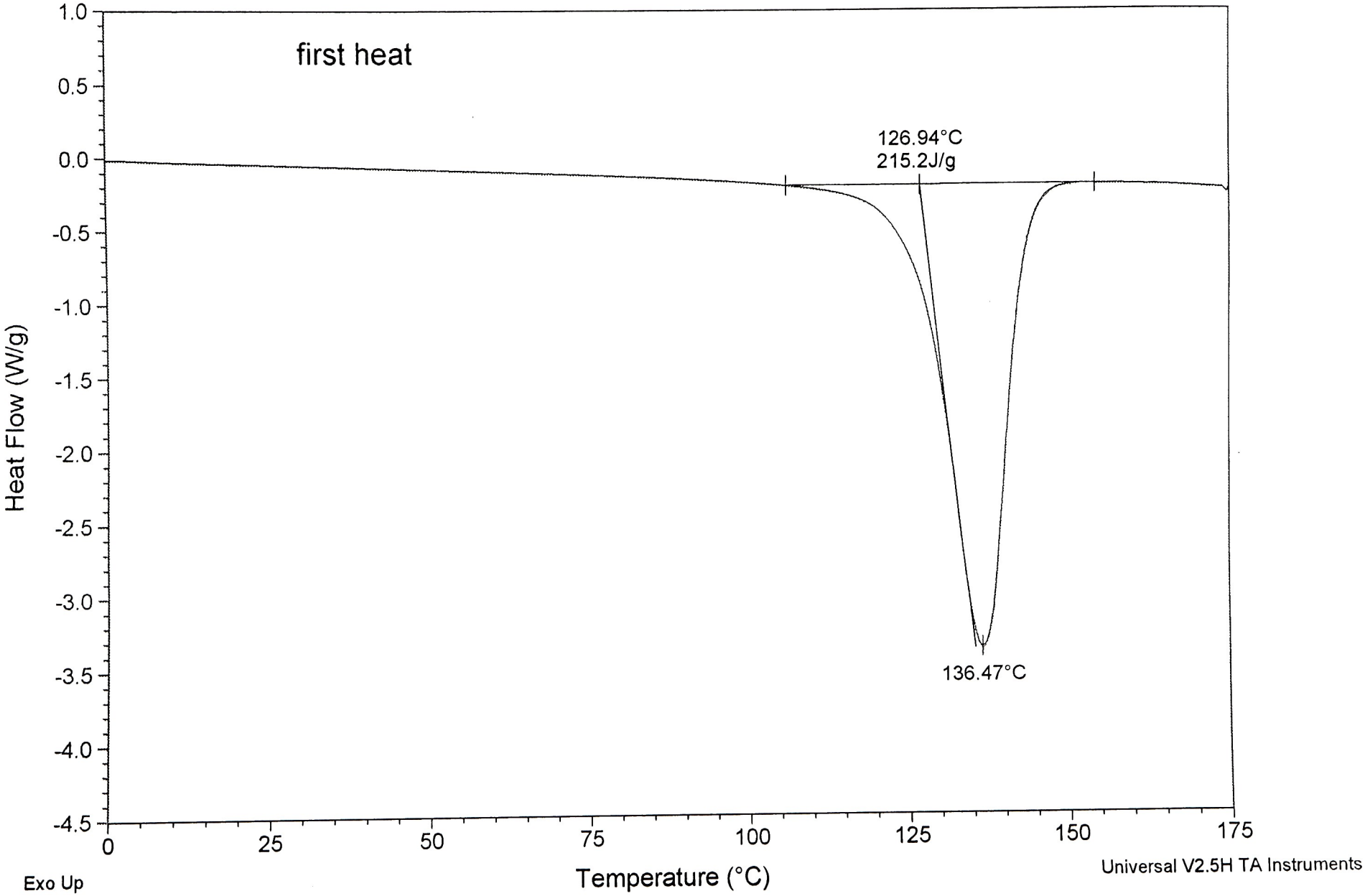

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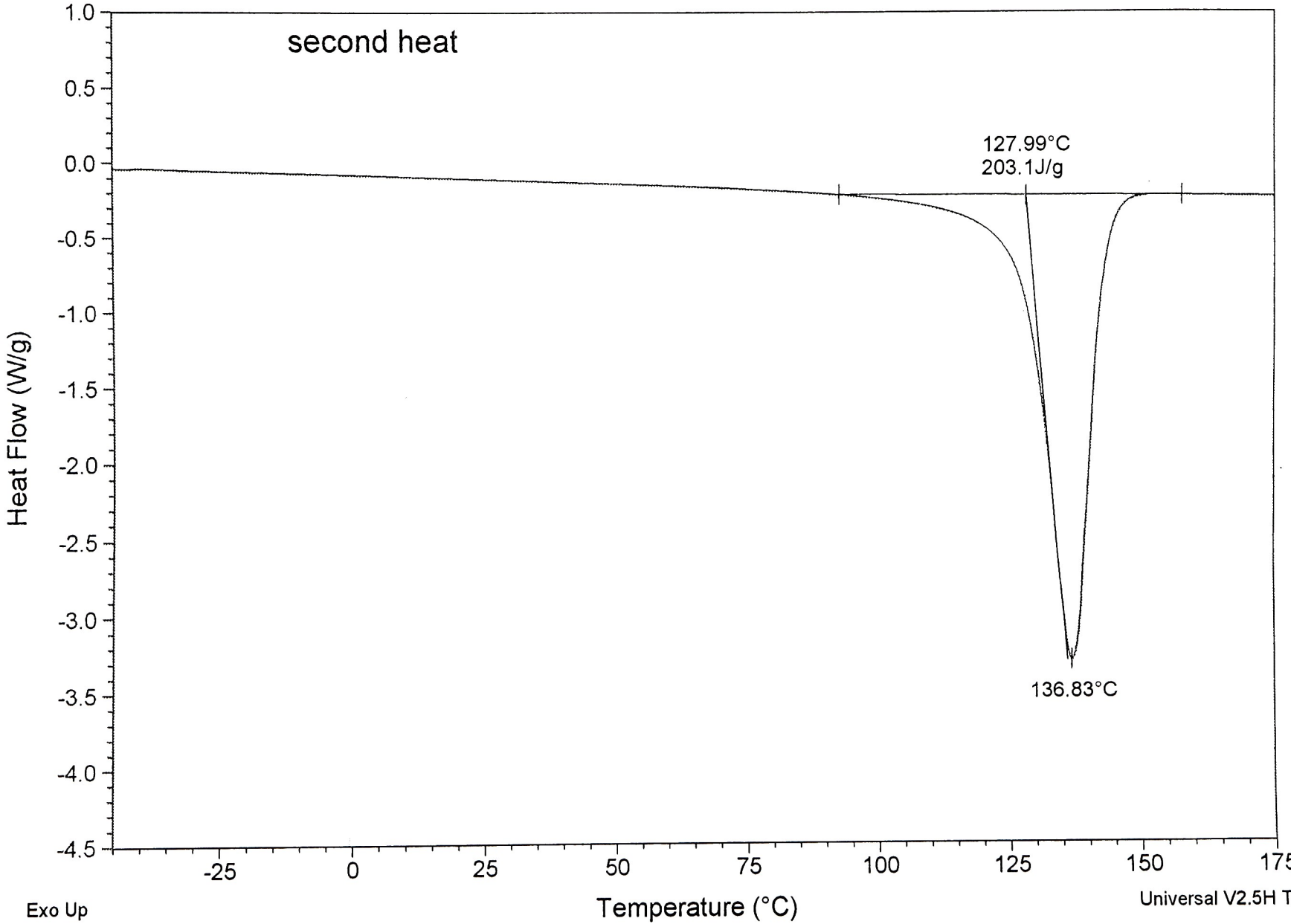

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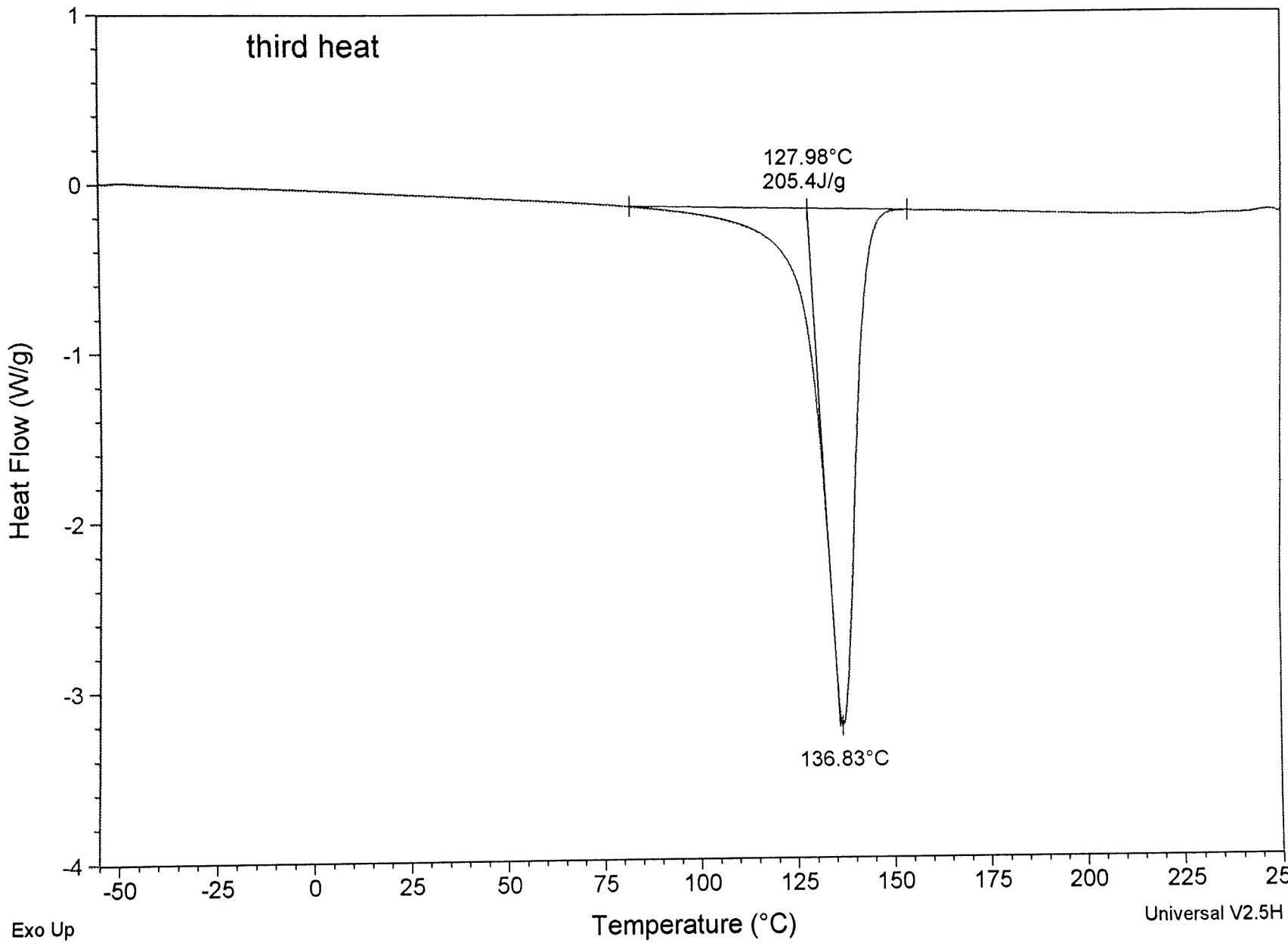

E/MA Cop 6

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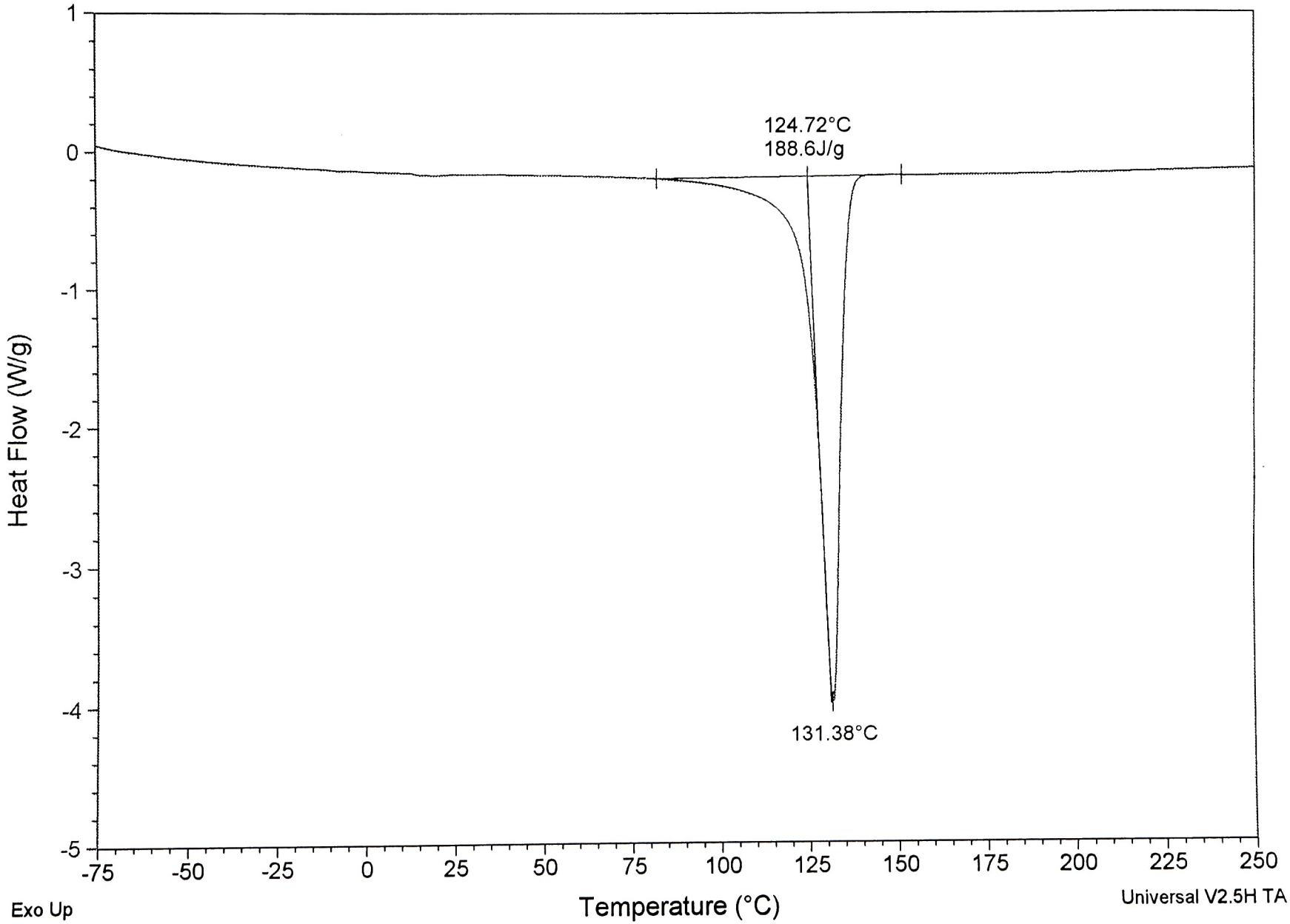

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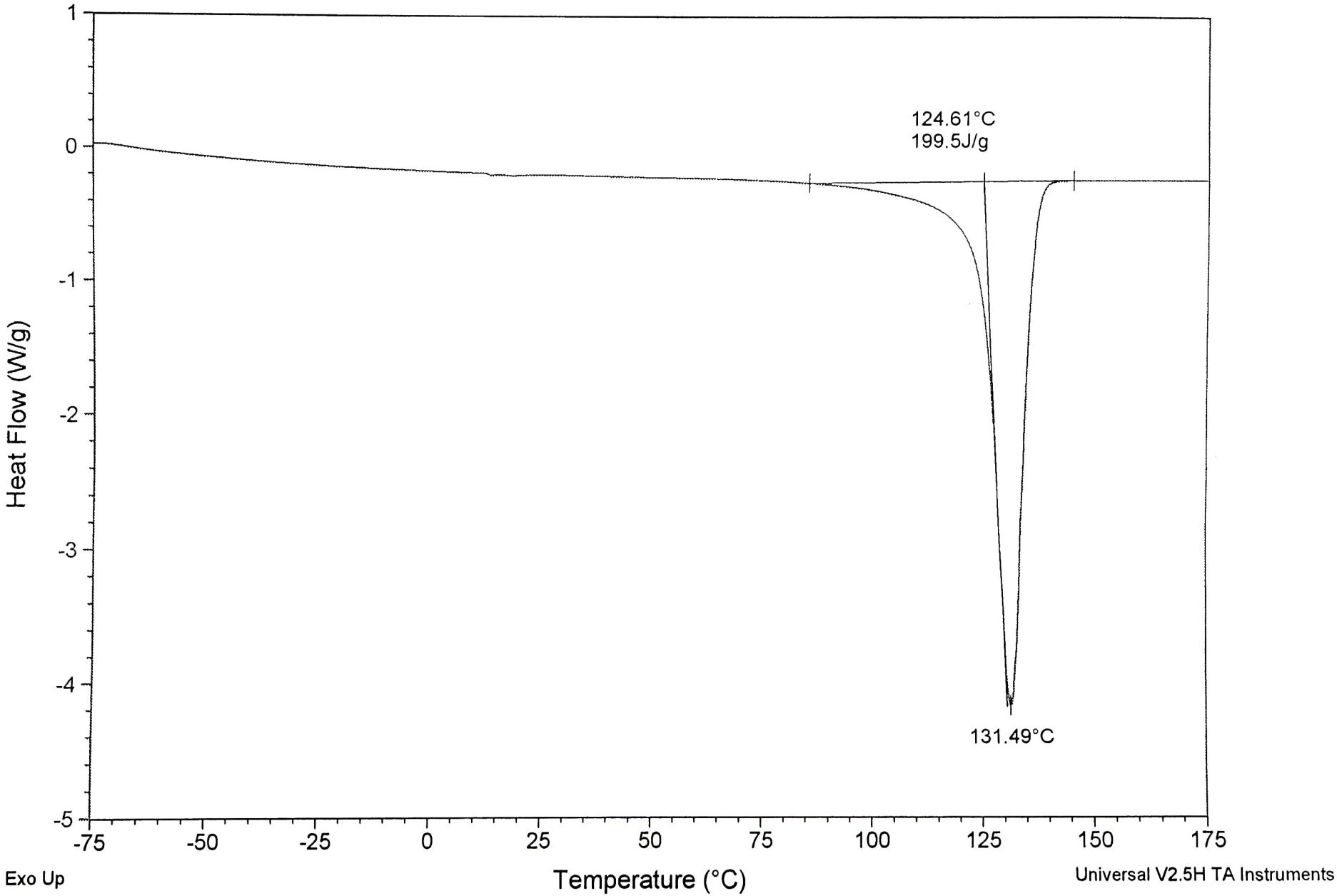

E/MA Cop 6

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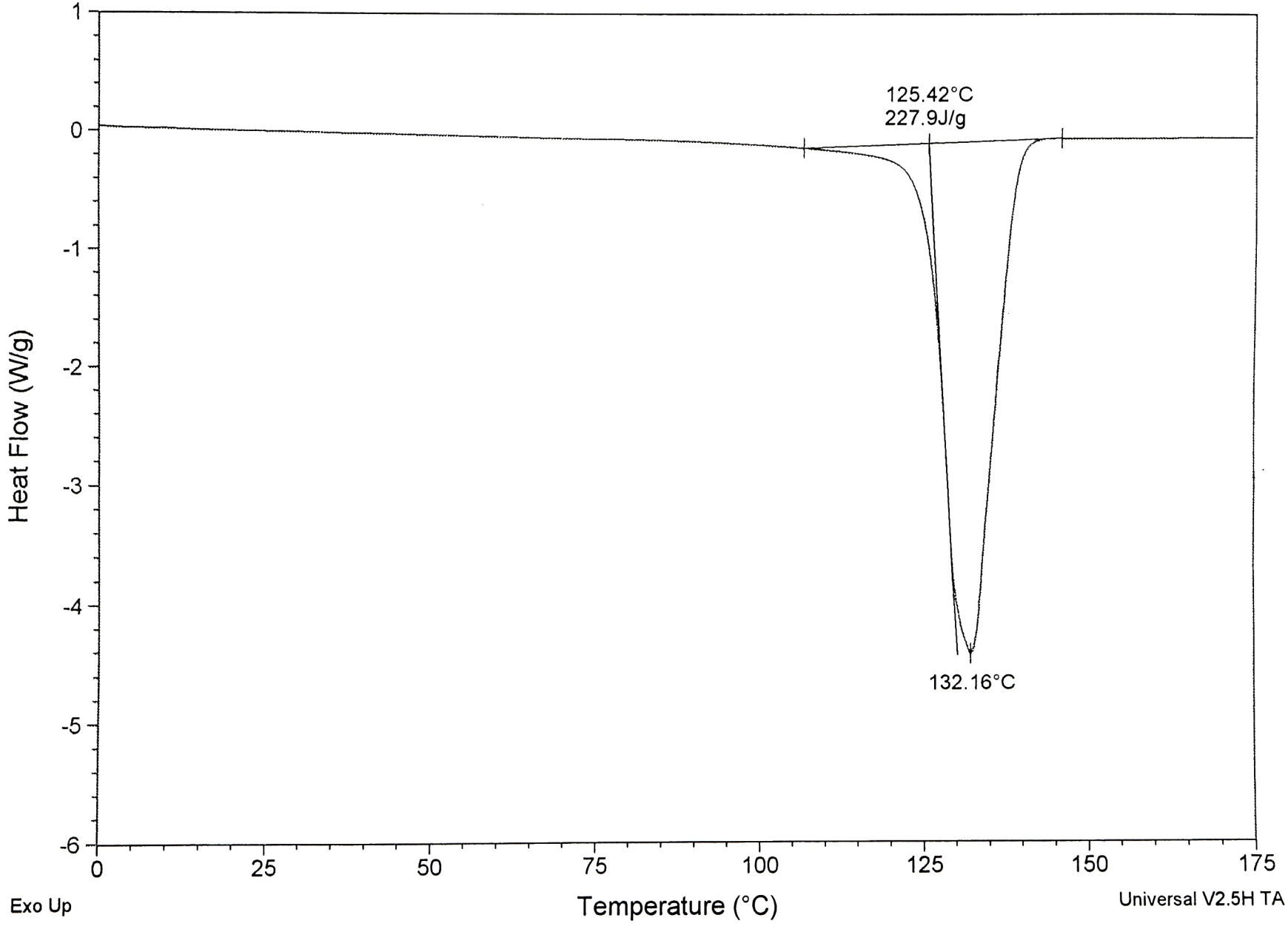

E/MA Cop 7

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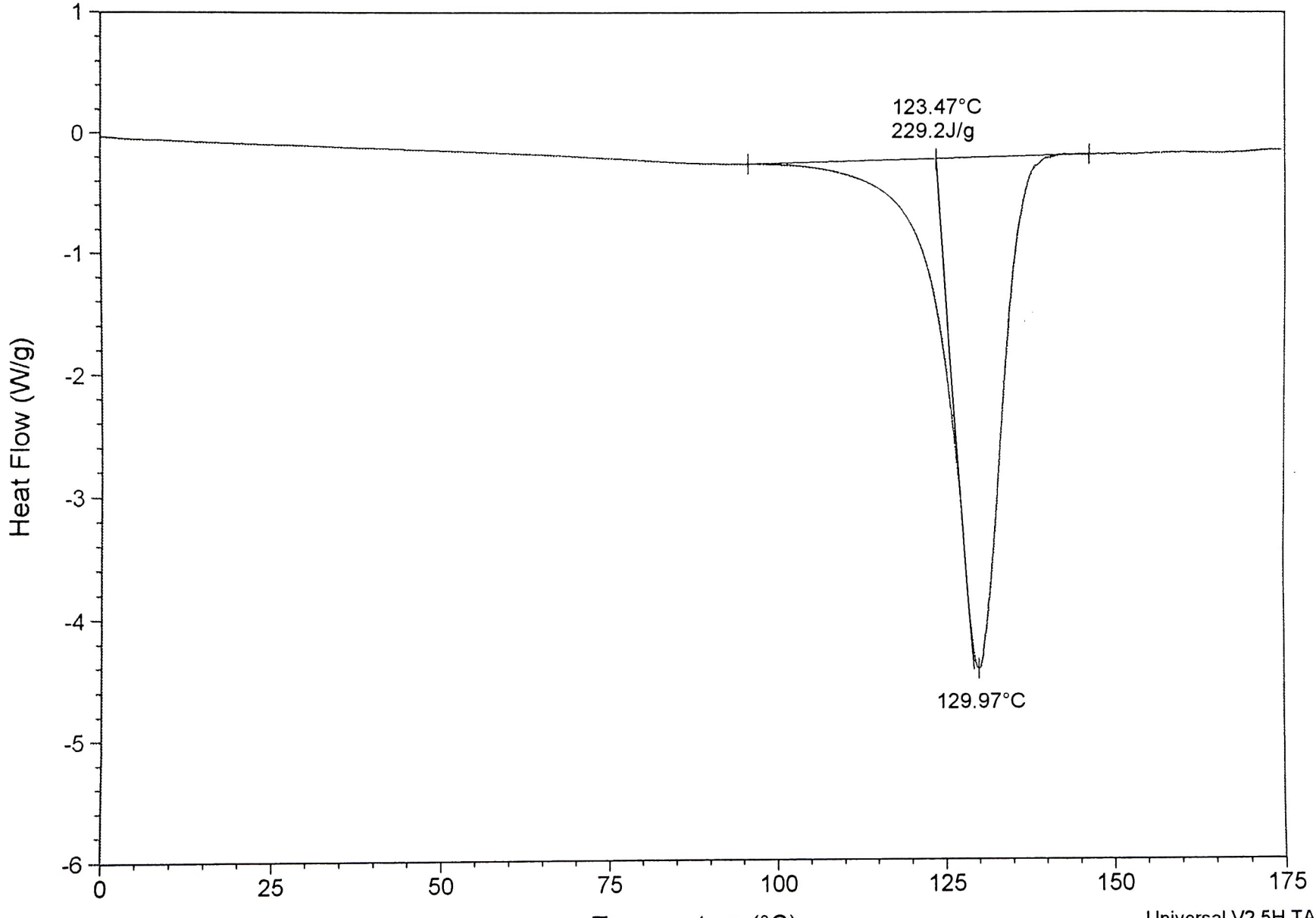

E/MA Cop 7

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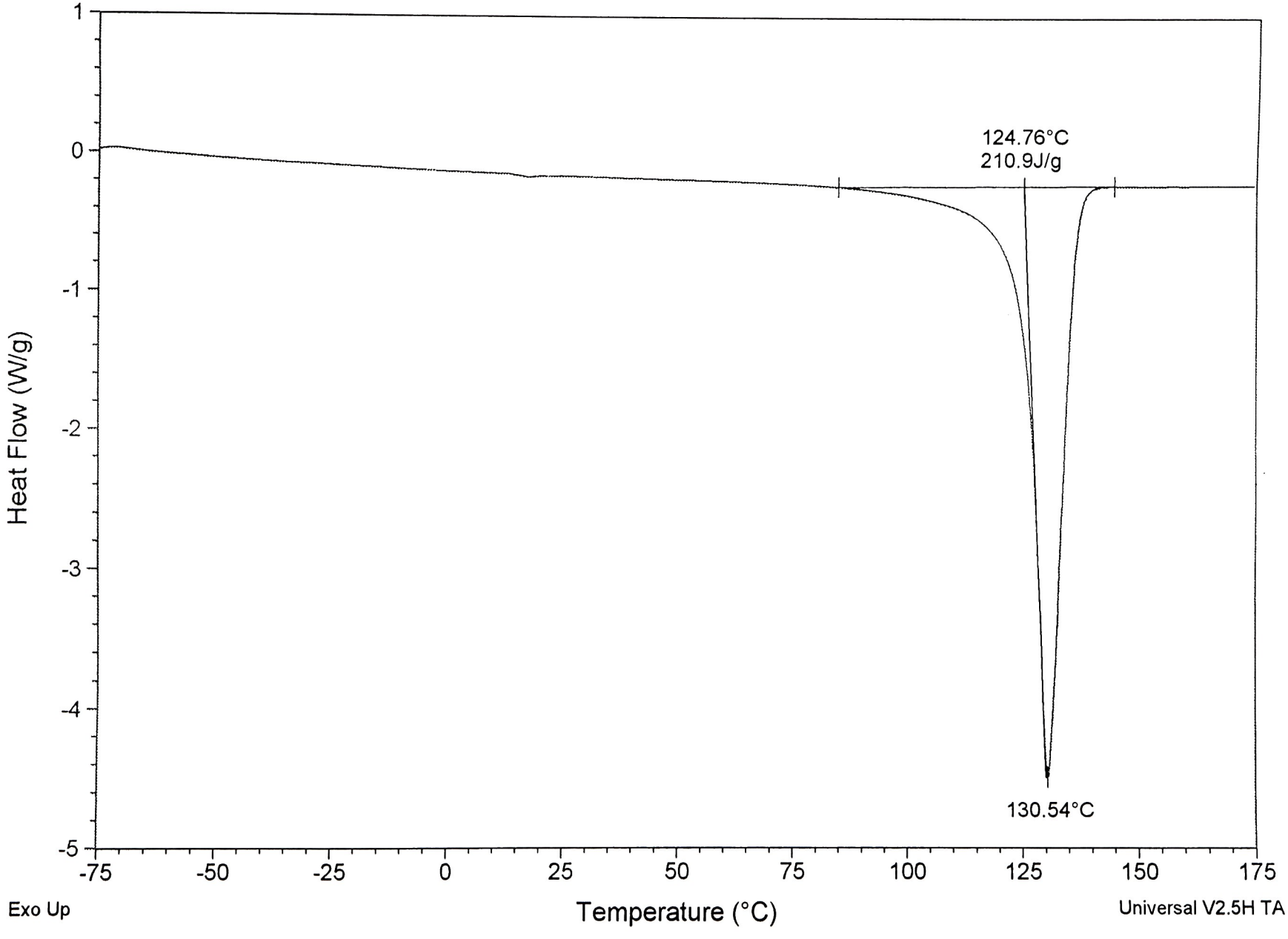

E/MA Cop7

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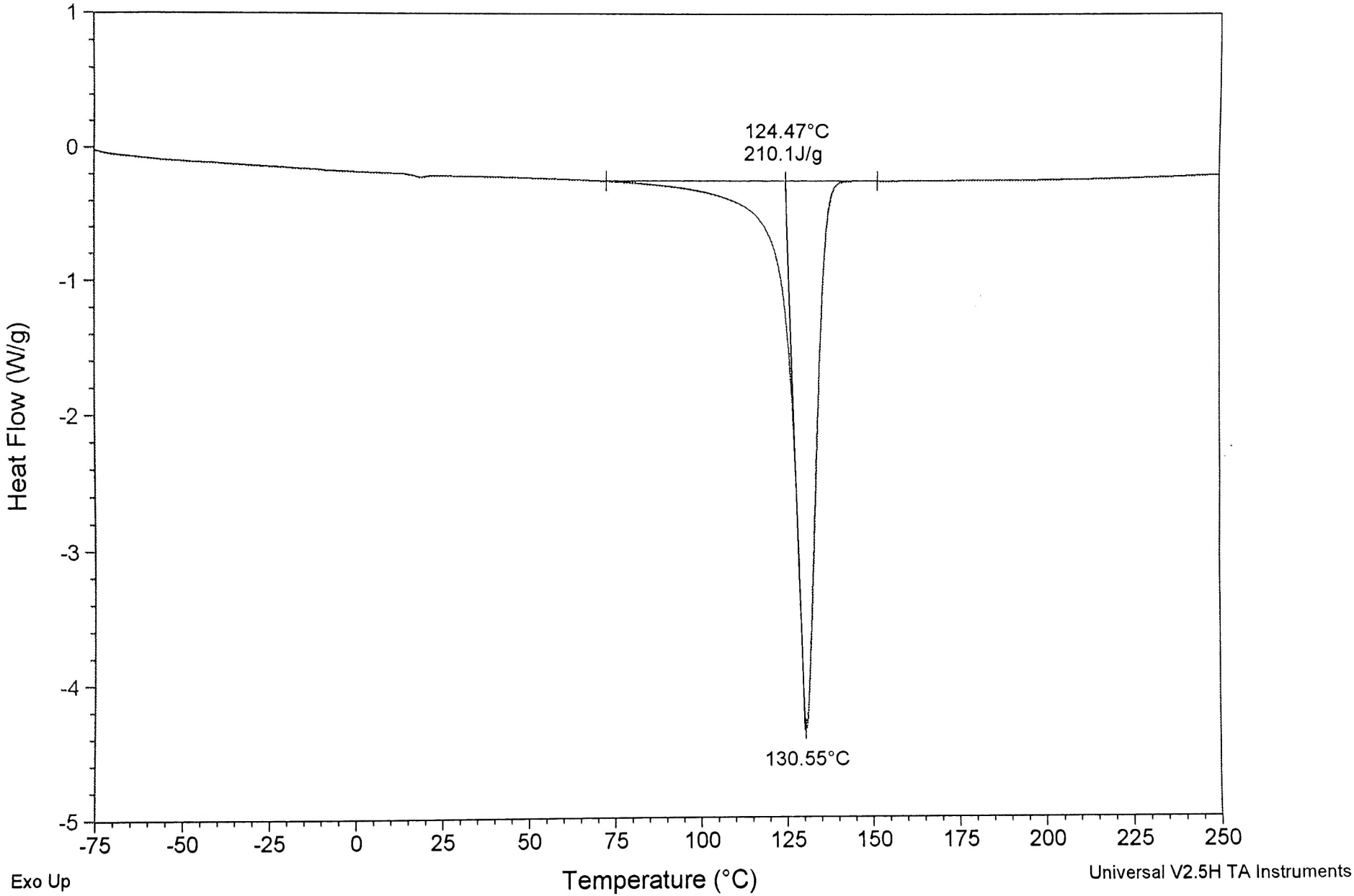

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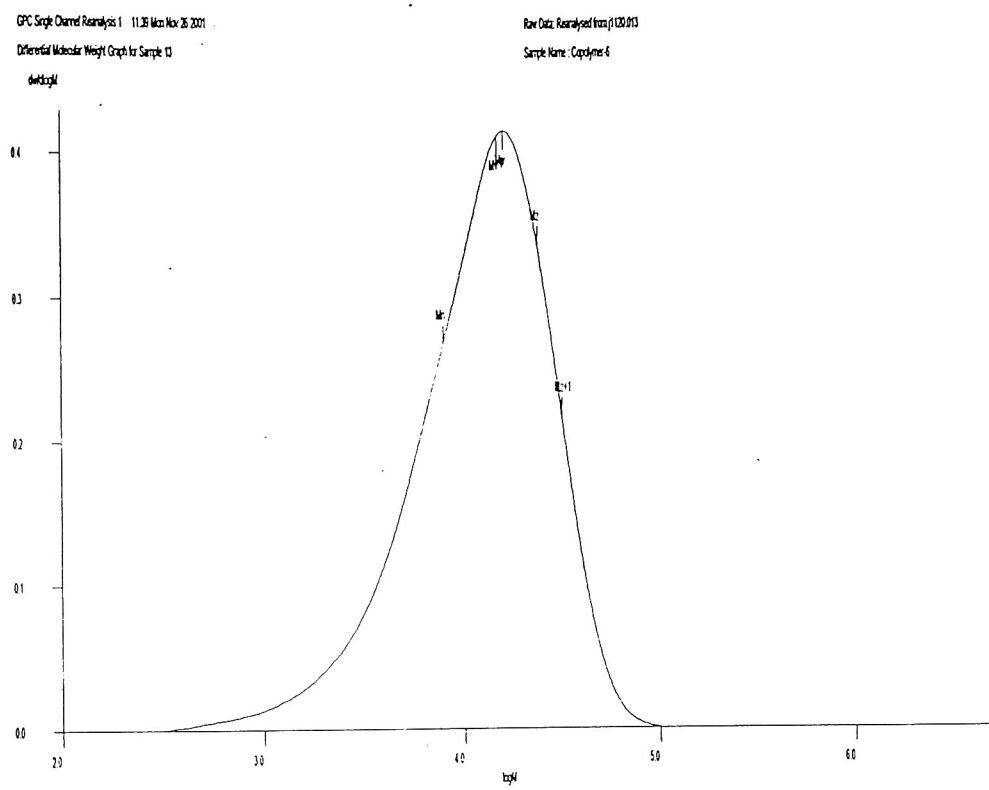
GPC Single Channel Reanalysis 1 11:35 Mon Nov 26 2001
Differential Molecular Weight Graph for Sample 13
Raw Data: Reanalysed from p1120.013
Sample Name : Copolymer 4
dwt/dlogM
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0.3
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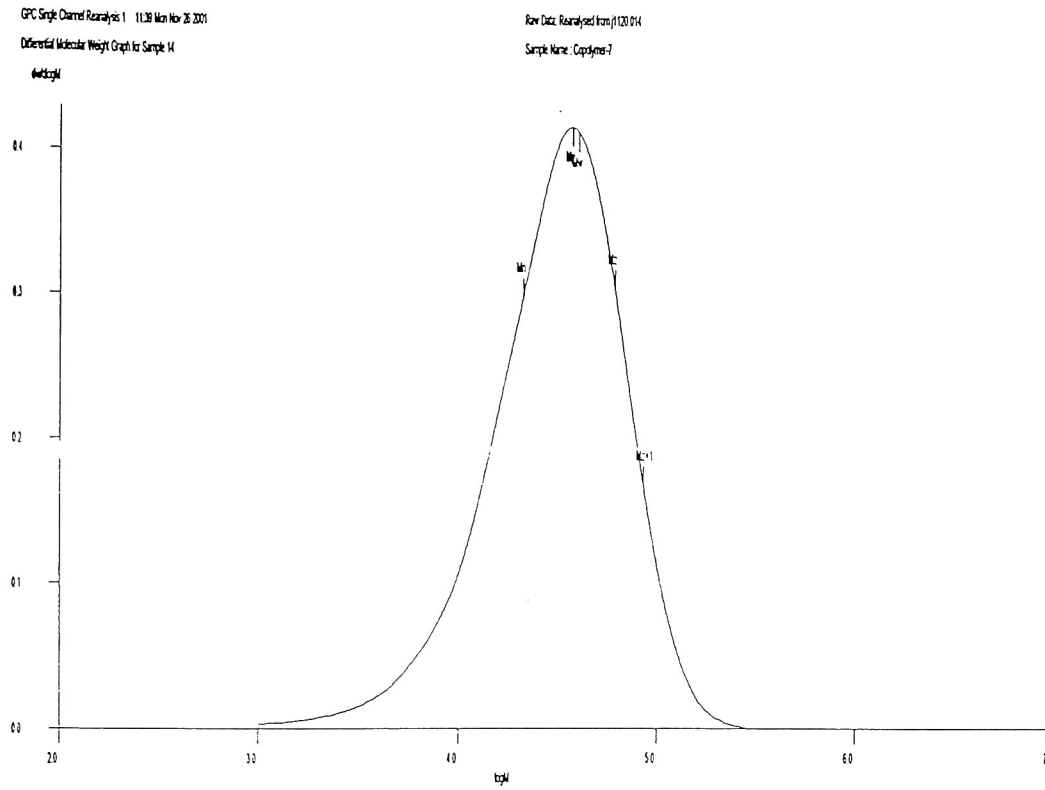
0.1
0.0
2.0
3.0
4.0
5.0
6.0
logM

E/MA Cop 4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0.0
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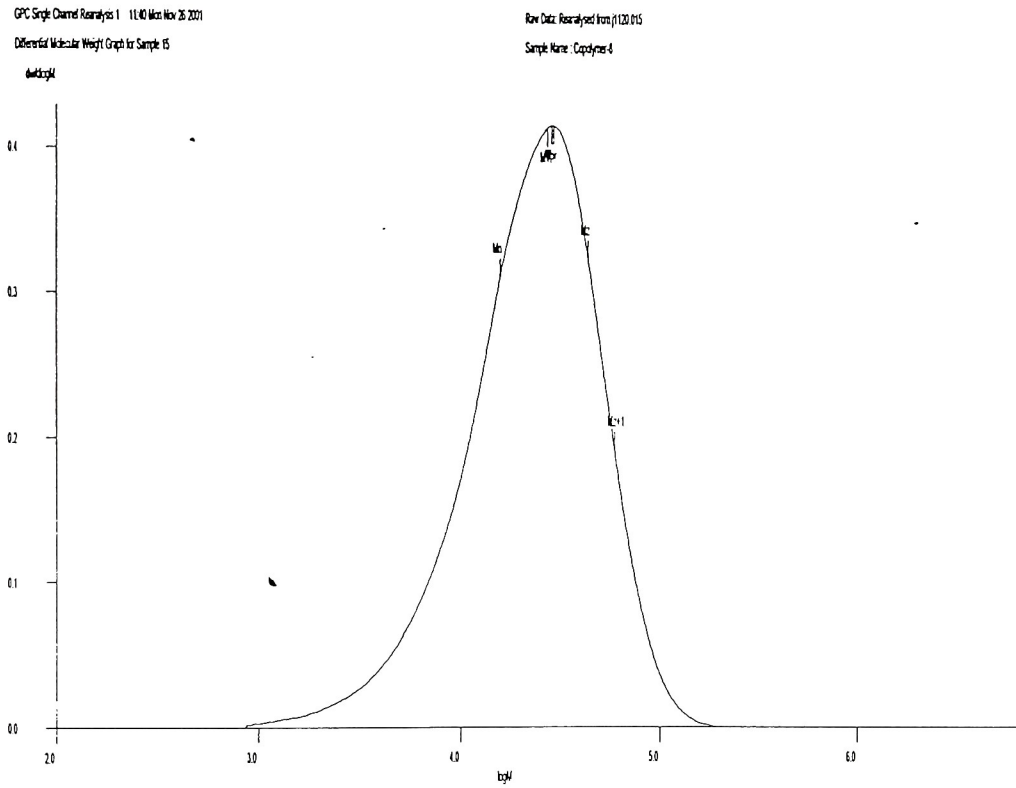
3.0
4.0
5.0
6.0

E/MA Cop 5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0.0
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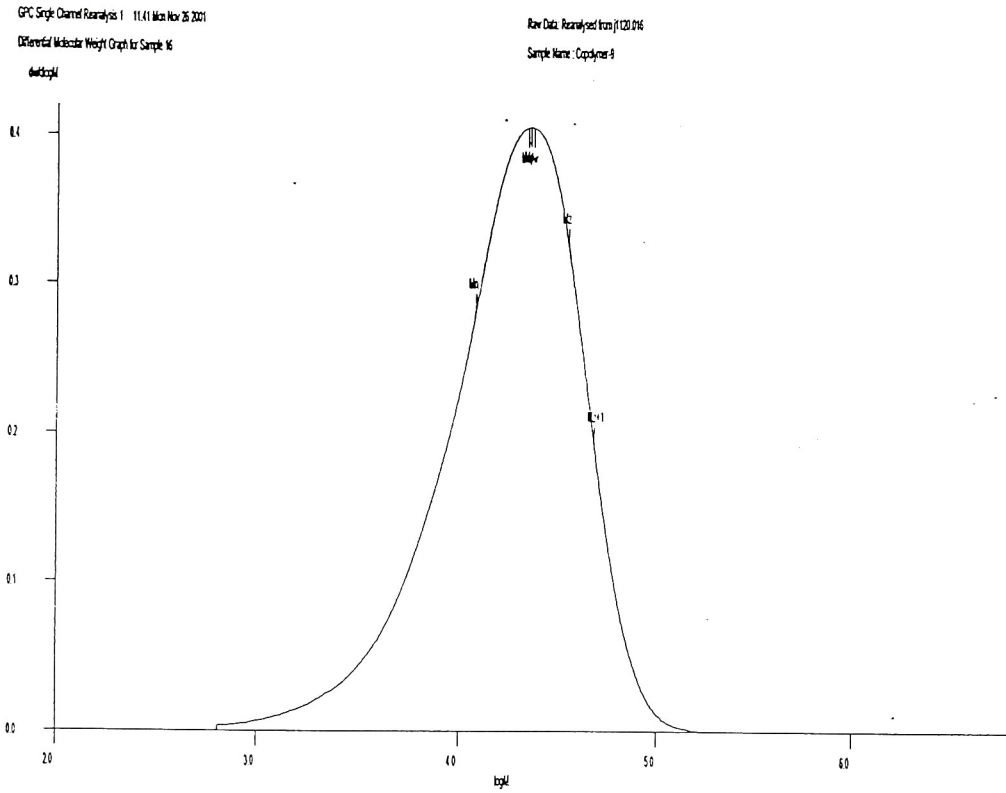
3.0
4.0
5.0
6.0
logM

E/MA Cop 6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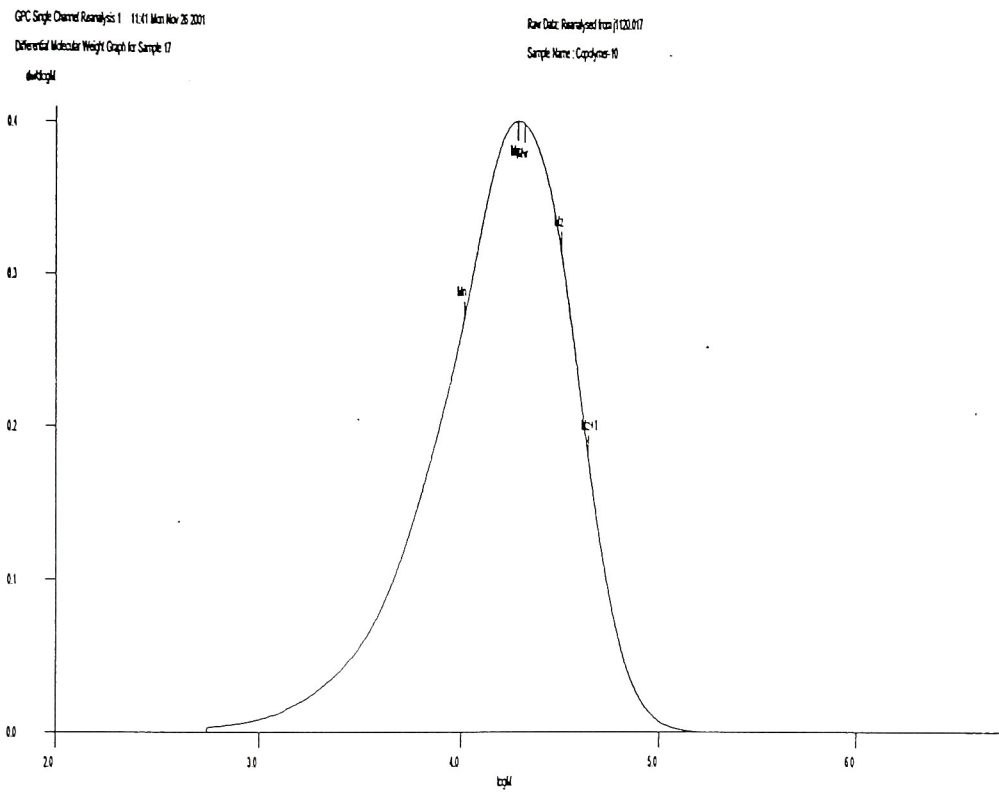
0.0
2.0
3.0
4.0
5.0
6.0

E/MA Cop 7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E/MA Cop 3

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tn	H1	dmf	200
at	4.000	dseq	
np	64000	dres	1.0
sw	8000.0	homo	n
fb	not used	temp	23.0
bs	4	PROCESSING	
tpwr	59	lb	0.30
pw	5.5	wtfile	
d1	6.000	proc	lp
tof	900.0	fn	65536
nt	128	math	f
ct	44		
alock	y	werr	
gain	24	wexp	save
FLAGS		wbs	
il	n	wnt	wft
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-0.2		
wp	5000.0		
vs	477		
sc	0		
wc	240		
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is	5165.72		
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rfp	3030.1		
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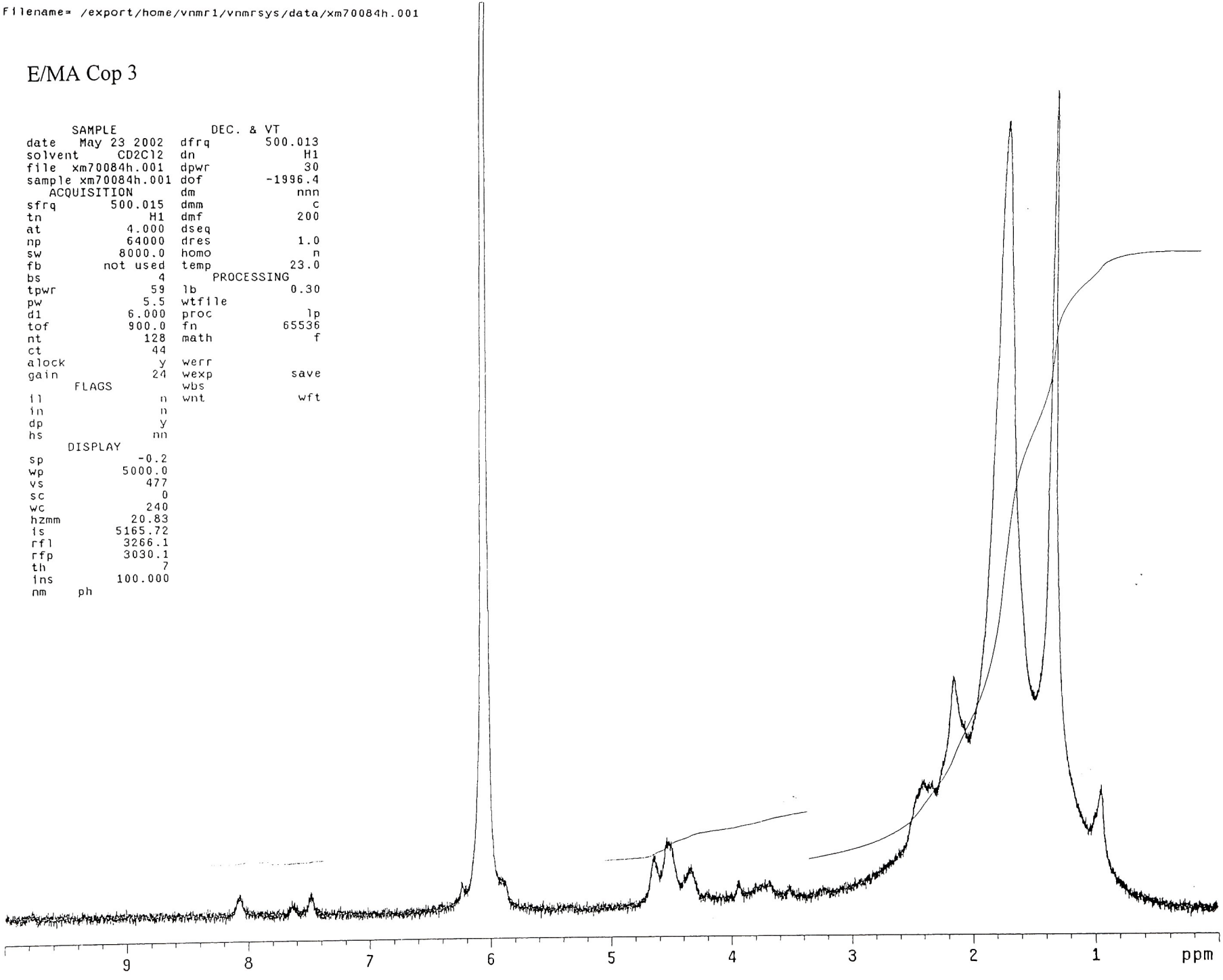
ins	100.000		
nm	ph		



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E/MA Cop 4*

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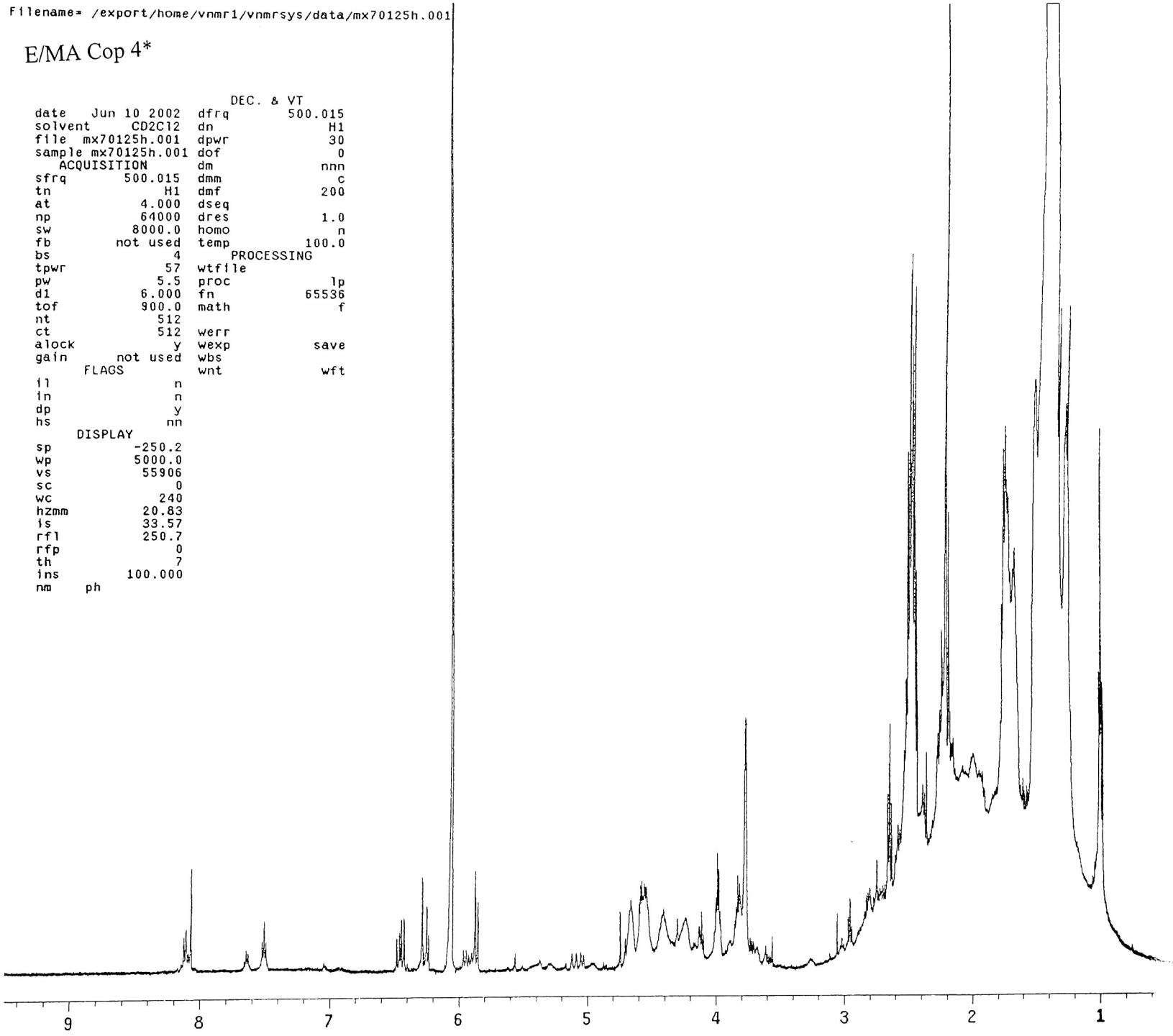
solvent	CD2Cl2	dn	H1
file	mx70125h.001	dpwr	30
sample	mx70125h.001	dof	0
	ACQUISITION	dm	nnn
sfrq	500.015	dmm	c
tn	H1	dmf	200
at	4.000	dseq	
np	64000	dres	1.0
sw	8000.0	homo	n
fb	not used	temp	100.0
bs	4		PROCESSING
tpwr	57	wtfile	
pw	5.5	proc	lp
d1	6.000	fn	65536
tof	900.0	math	f
nt	512		
ct	512	werr	
alock	y	wexp	save
gain	not used	wbs	
	FLAGS	wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
	DISPLAY		
sp	-250.2		
wp	5000.0		
vs	55906		
sc	0		
wc	240		
hzmm	20.83		
is	33.57		
rfl	250.7		
rfp	0		
th	7		
ins	100.000		
nm	ph		



Filename= /export/home/vnmr1/vnmrsys/data/xm70085h.002

E/MA Cop 5

SAMPLE		DEC. & VT	
date	May 29 2002	dfrq	500.015
solvent	CD2Cl2	dn	H1
file	xm70085h.002	dpwr	30
sample	xm70085h.002	dof	0
ACQUISITION		dm	nnn
sfrq	500.015	dmm	c
tn	H1	dmf	200
at	4.000	dseq	
np	64000	dres	1.0
sw	8000.0	homo	n
fb	not used	temp	100.0
bs	4	PROCESSING	
tpwr	59	lb	0.30
pw	5.5	wtfile	
d1	6.000	proc	lp
tof	900.0	fn	65536
nt	128	math	f
ct	128		
alock	y	werr	
gain	not used	wexp	save
FLAGS		wbs	
il	n	wnt	wft
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	6000.0		
vs	25329		
sc	0		
wc	240		
hzmm	25.00		
is	486.70		
rfl	250.9		
rfp	0		
th	7		
ins	100.000		
nm	ph		

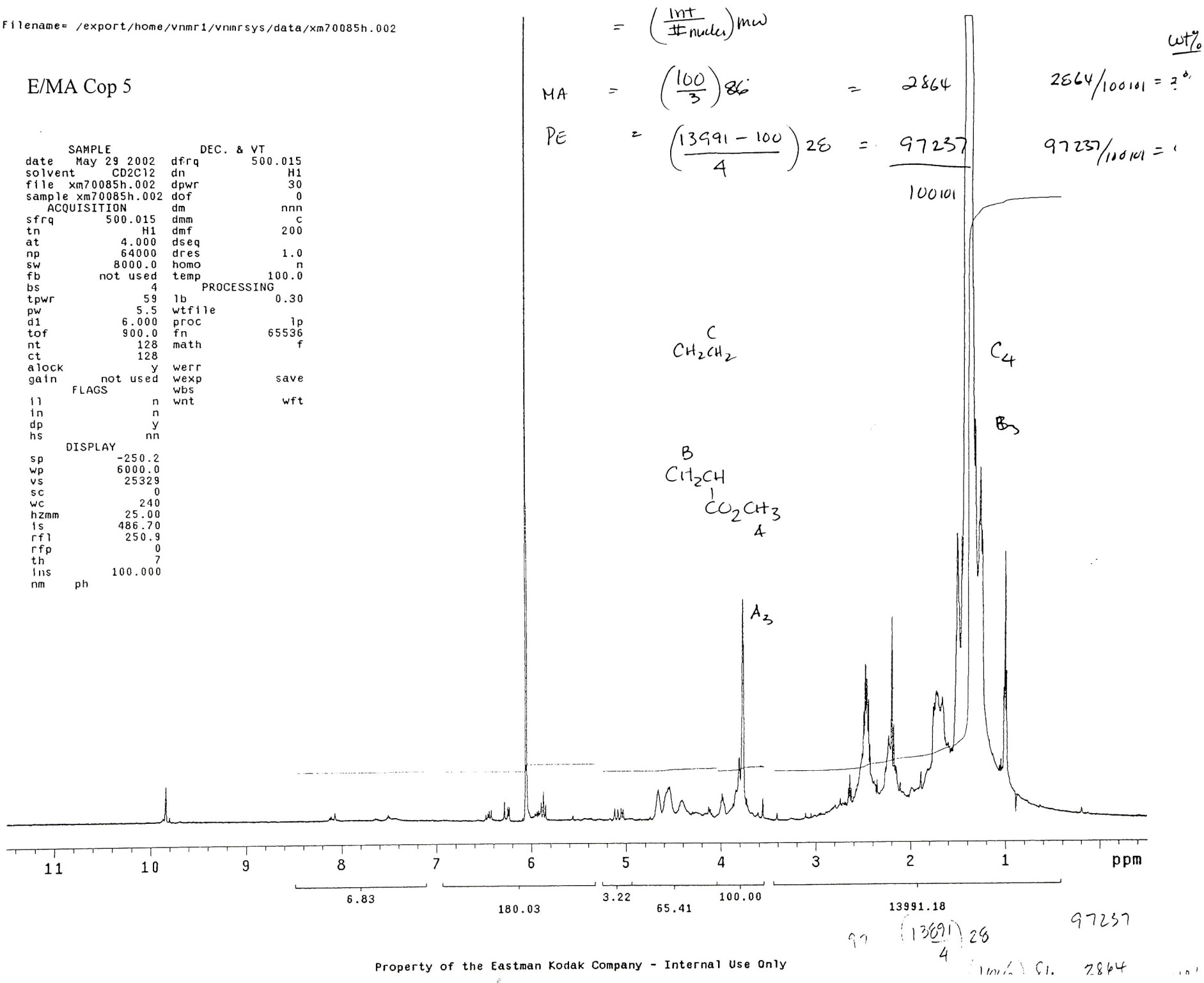
$= \left(\frac{\text{Int}}{\#\text{nuclei}}\right) mw$

wt%

MA $= \left(\frac{100}{3}\right) 86 = 2864$ $\quad 2864/100101 = 3\%$

PE $= \left(\frac{13991 - 100}{4}\right) 28 = 97237$ $\quad 97237/100101 = 9$

100101

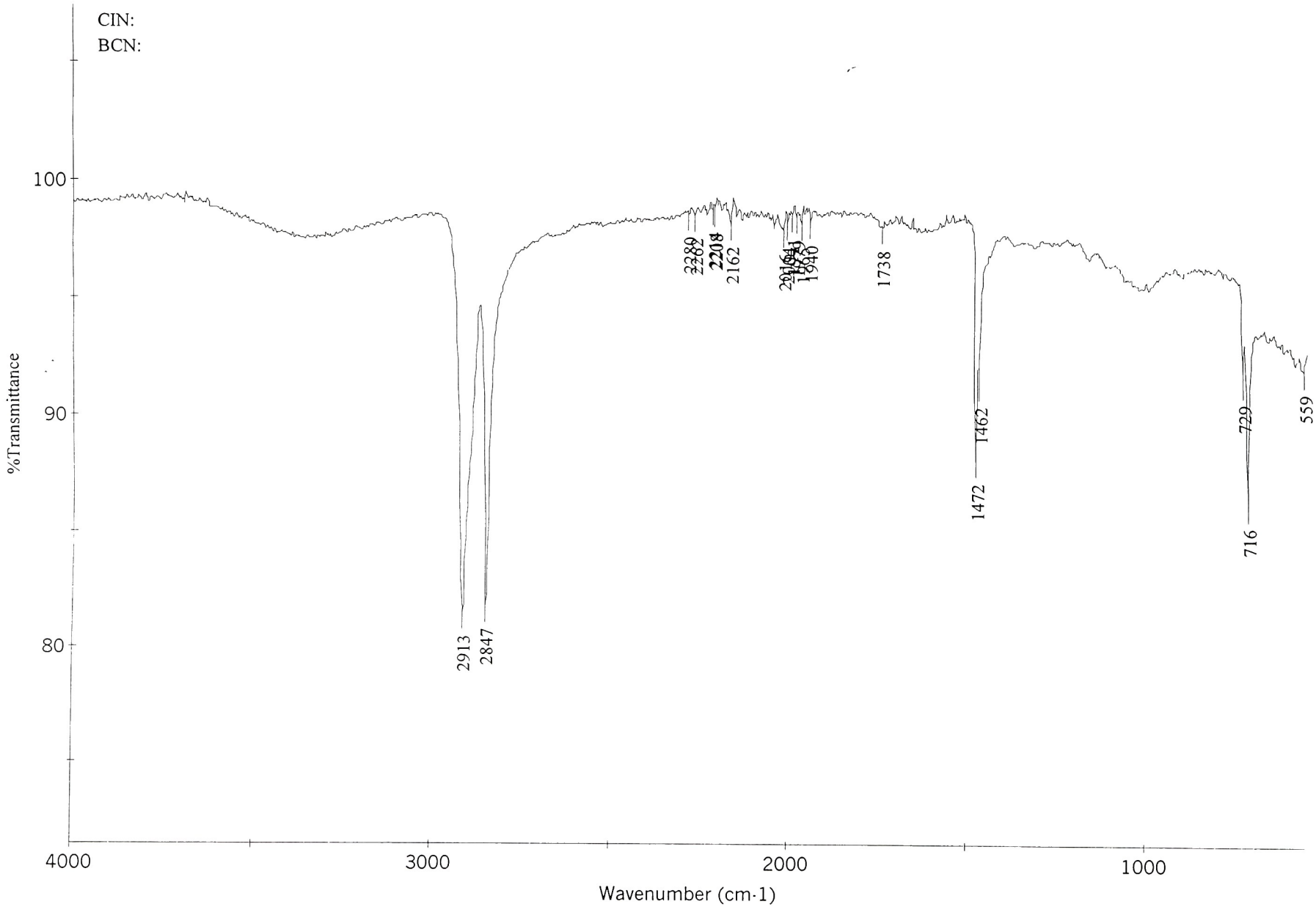


97237

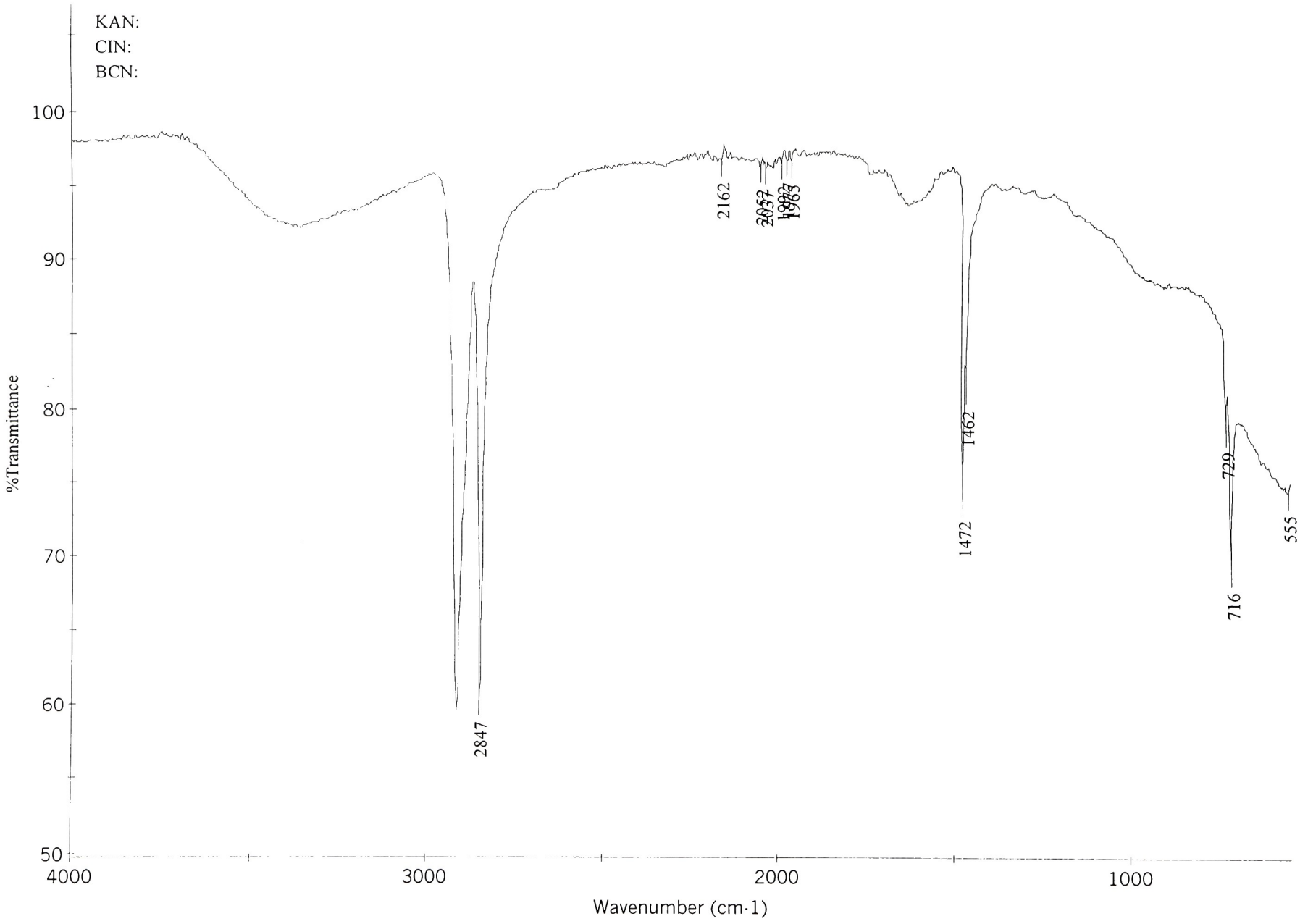
$\left(\frac{13991}{4}\right) 28$

7864

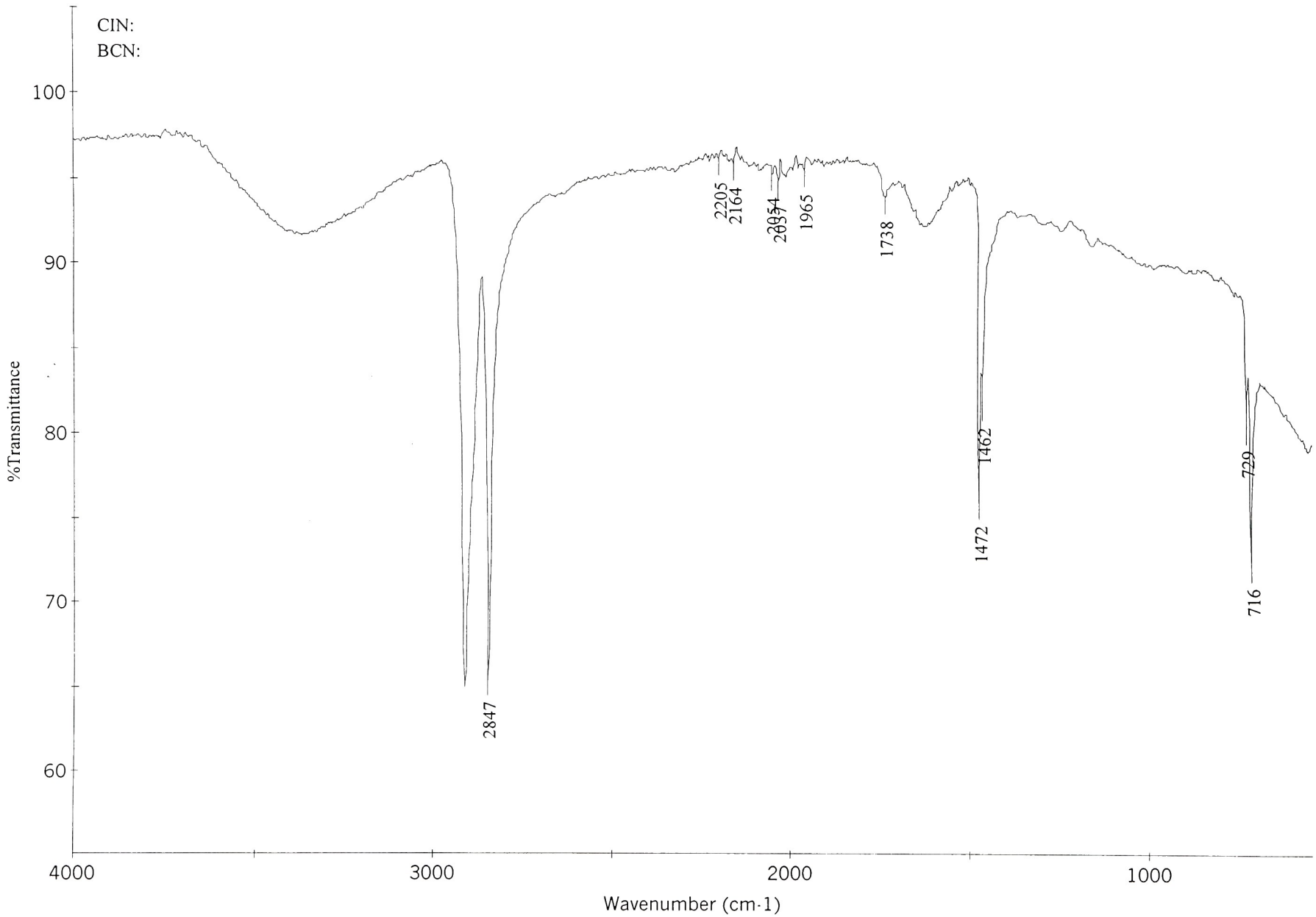
E/MA Cop 1



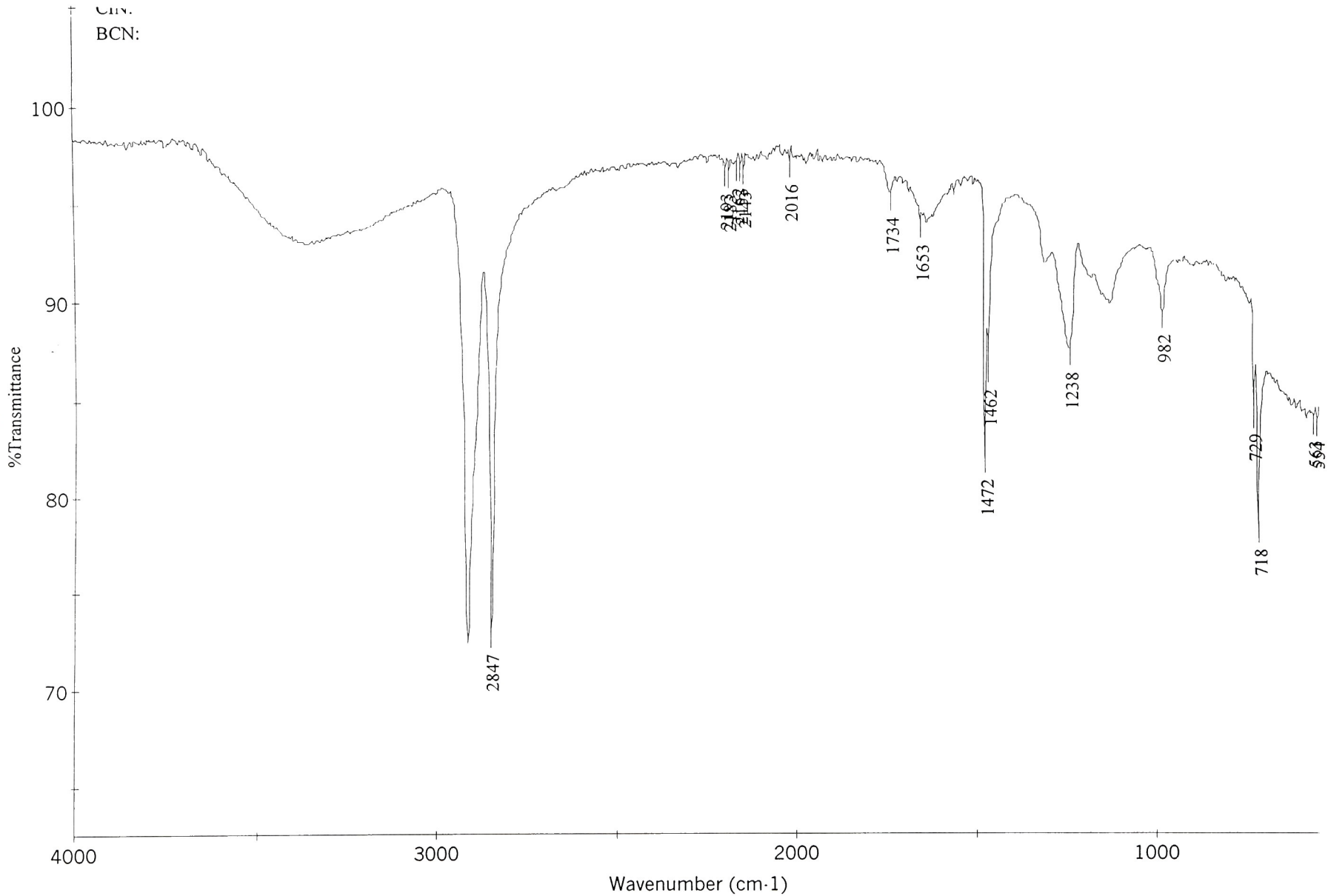
E/MA Cop 2



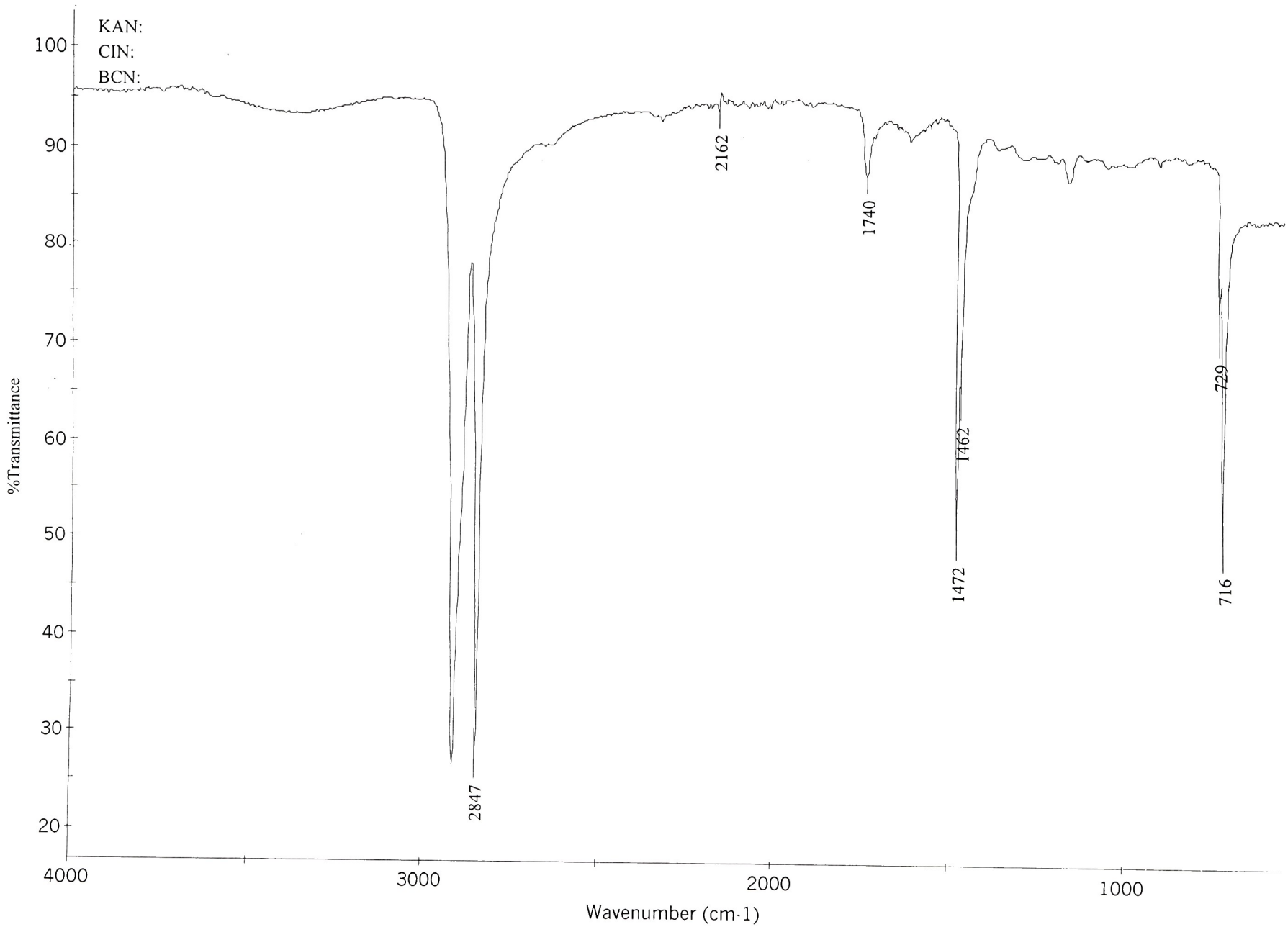
E/MA Cop 3



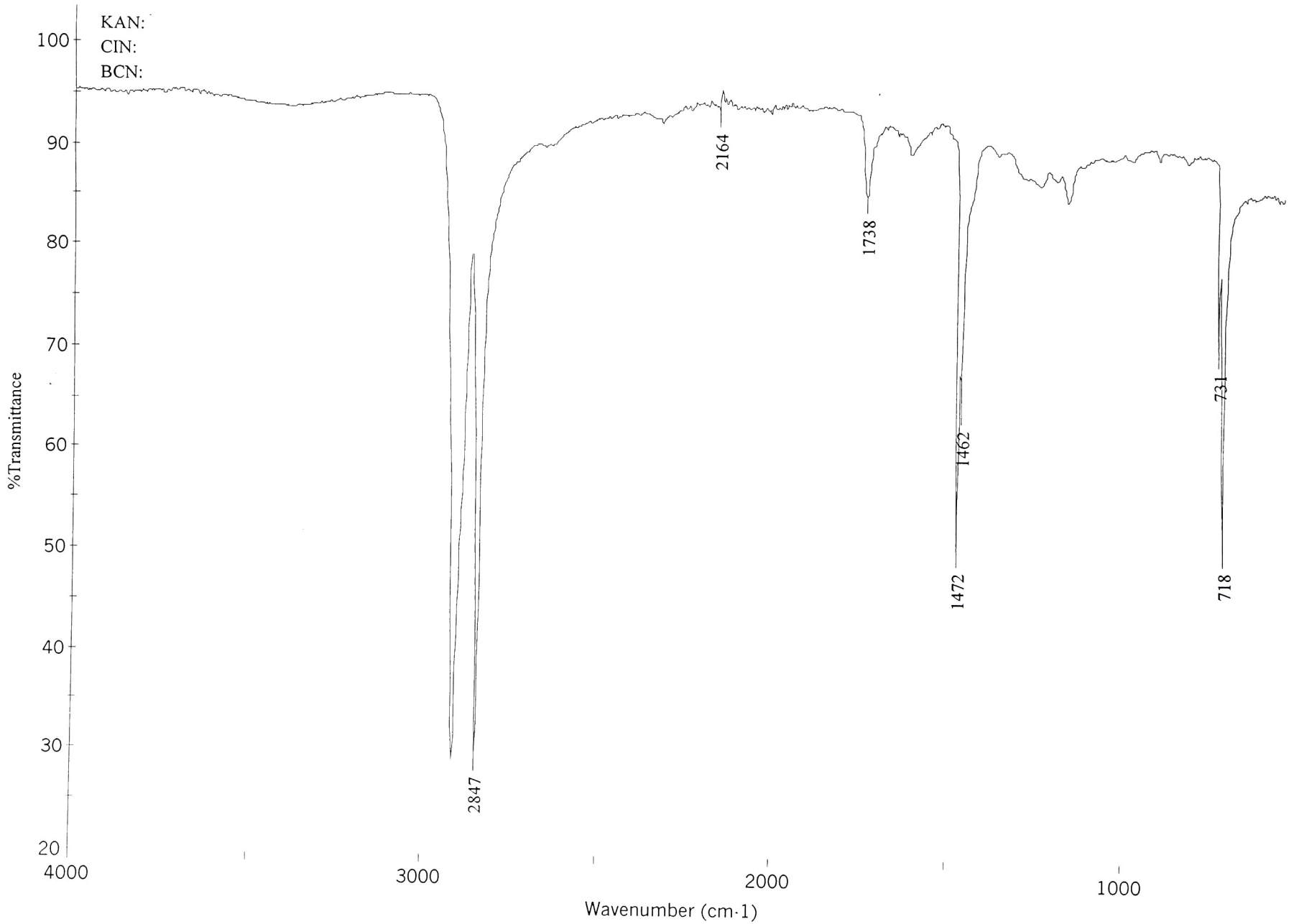
E/MA Cop 4*

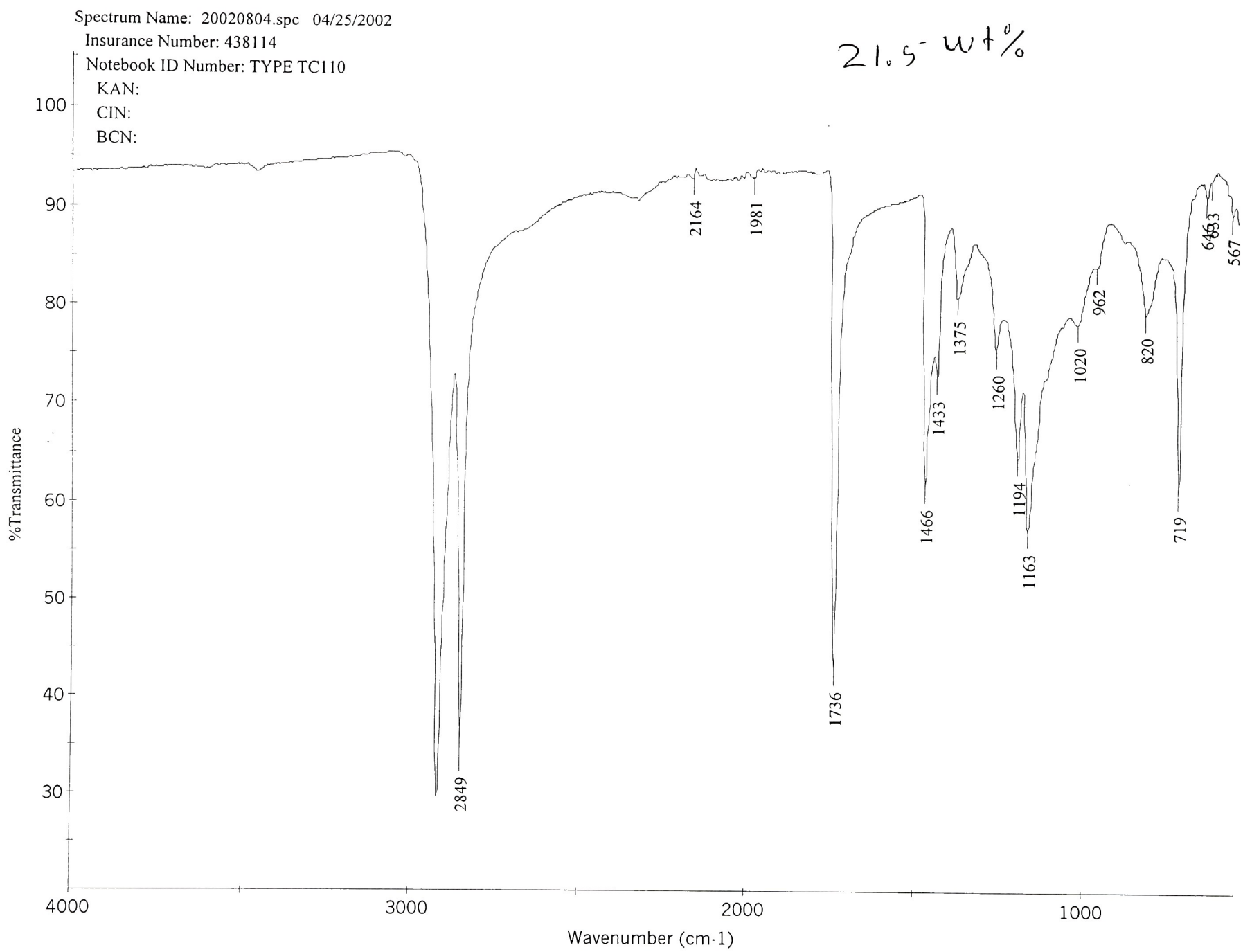


E/MA Cop 5



E/MA Cop 6





Comments:

Spectrum Name: 20020805.spc 04/25/2002

Insurance Number: 438114

Notebook ID Number: TYPE TC220

KAN:

CIN:

BCN:

24 wt%

9.3 mol%